

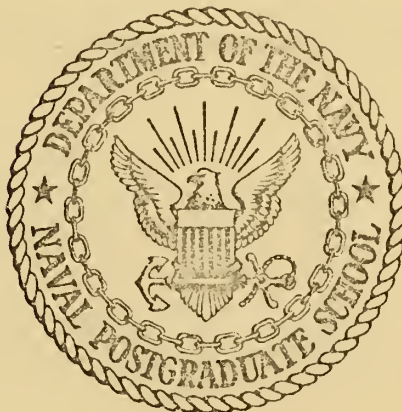
A STUDY OF NUTRIENT VARIATIONS IN THE SURFACE
AND MIXED LAYER OF MONTEREY BAY
USING AUTOMATIC ANALYSIS TECHNIQUES

Gaylord Oneil Paulson

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Monterey, California



THESIS

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AND MIXED LAYER OF MONTEREY BAY
USING AUTOMATIC ANALYSIS TECHNIQUES

by

Gaylord Oneil Paulson

Thesis Advisor:

N. E. J. Boston

September 1972

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A Study of Nutrient Variations in the Surface
and Mixed Layer of Monterey Bay
Using Automatic Analysis Techniques

by

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Lieutenant Commander, United States Navy
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ABSTRACT

Concentrations of silicate, phosphate, nitrate, and nitrite were determined in Monterey Bay, California. Data were collected aboard ship during four cruises in April and May 1972 using the Technicon[®] AutoAnalyzer[®] II System in dual channel operation. The sensitivity, reproducibility, and accuracy of this system were investigated and the results presented. Nutrient concentrations were presented as surface variations, depth variations, and vertical profiles. The large variability of nutrient concentrations in the ocean area studied was discussed. Upwelling areas were investigated for nutrient concentrations, circulation patterns, and variations in nutrient ratios. Planktonic bloom areas have been identified from the low nutrient levels, low nutrient ratio values, and high chlorophyll correlations. Results indicate that silicate was the limiting nutrient to biological activity in the waters studied. Assimilation ratios for biological activity were found to be 16.33 for $\text{NO}_3:\text{PO}_4$ and 21.14 for $\text{SiO}_4:\text{PO}_4$. Nutrient plateau regions were analysed and sources discussed. The major cause of nutrient concentration changes in the area (except plankton blooms) as determined from nutrient ratio studies was found to be circulation of the water masses.

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Technicon Industrial Corporation deserves special mention. Mr. Robert M. Gasco was quite helpful and always willing to discuss any equipment difficulties. He authorized the use of Technicon procedures and drawings in this paper.

I. INTRODUCTION

The three major nutrients in sea water (nitrate, phosphate, and silicate) have been analysed and studied for many years [Riley and Skirrow 1965]. Large volumes of data have been collected of nutrient concentrations from all the world oceans.

Until recently most observations were obtained from manual chemical analyses performed in laboratories ashore. This necessitated a significant sample storage time in transit during which most investigators attempted to prevent nutrient changes by freezing the samples. Whether this practice actually prevents all nutrient changes is still questionable. Collection has normally been accomplished using the traditional method of bottle sampling tens of meters apart in depth and with casts spaced a few (or a few hundred) miles apart.

Nutrient concentrations in the open oceans have been found to be quite variable [Riley and Skirrow 1965]. This variability is caused by both biological and physical effects. There is a lack of significant data from coastal regions, but in these waters the nutrient variability is even greater than found in the open oceans due to complex circulation patterns and the patchiness of biological activity [Margalef 1970]. These complex influences tend to complicate the nutrient variations such that when using

traditional sampling techniques correlations have been difficult to obtain. Sampling procedures were required which would give better spacial resolution than previously obtained. Furthermore, the rapidity of nutrient changes are such that much shorter time lapses between sampling and analysis and shorter time intervals between samples were desired in order to produce statistically meaningful results. Hence, shipboard operations were necessary in order to reduce storage and handling effects and allow for near real-time determinations to be obtained.

In an attempt to improve the quality and increase the rapidity of nutrient concentration determinations during shipboard analysis automatic analysis techniques have been developed and tested [Brewer and Riley 1965, Grasshoff 1965, Chan and Riley 1966, Molof et al. 1966]. Technicon® Instruments Corporation produced an automated analytical system (called the AutoAnalyzer® I (AA-I) system) whereby nutrient concentrations were colorimetrically determined [Strickland and Parsons 1968, Atlas et al. 1971]. Recently, a second generation AutoAnalyzer® II (AA-II) system has been developed. This system is significantly different from the AA-I system and uses improved components and modified procedures.

This study was performed to determine the capabilities of the AA-II system, test and/or develop analytical procedures and techniques for shipboard operation, and study the nutrient variations in the photic zone of the ocean in the area of Monterey, California.

II. INSTRUMENTATION

A Technicon[®] AutoAnalyzer[®] II system was used to measure nutrient concentrations. The basic components of the AutoAnalyzer[®] system will be discussed following the physical arrangement shown in Figure 1.

A. SAMPLER

This sampler has a 40 sample-cup tray capacity and two wash receptacles. Cups are available in various sizes. Five ml sample cups were used exclusively during this study. A sample probe, installed in a movable arm, aspirates the samples into the analytical system. Between each sample a segment of wash solution aids in cleaning the system and in segregating the samples. An interchangeable timing cam is located in the sampler to control the time allotted for sampling each cup and for aspirating wash solution between samples. For dual operation of nutrient analysis, a sampling rate of 40 samples/hour with a sample-to-wash ratio of 4:1 was found satisfactory for all four analysis procedures.

B. PUMP

This peristaltic proportioning pump was used to pump all reagents, wash, samples, and air into the analytical stream. It operates at a constant speed driving a roller system which, when forced against pump tubes, produces a constant flow through the tubes. The rate of flow is determined by

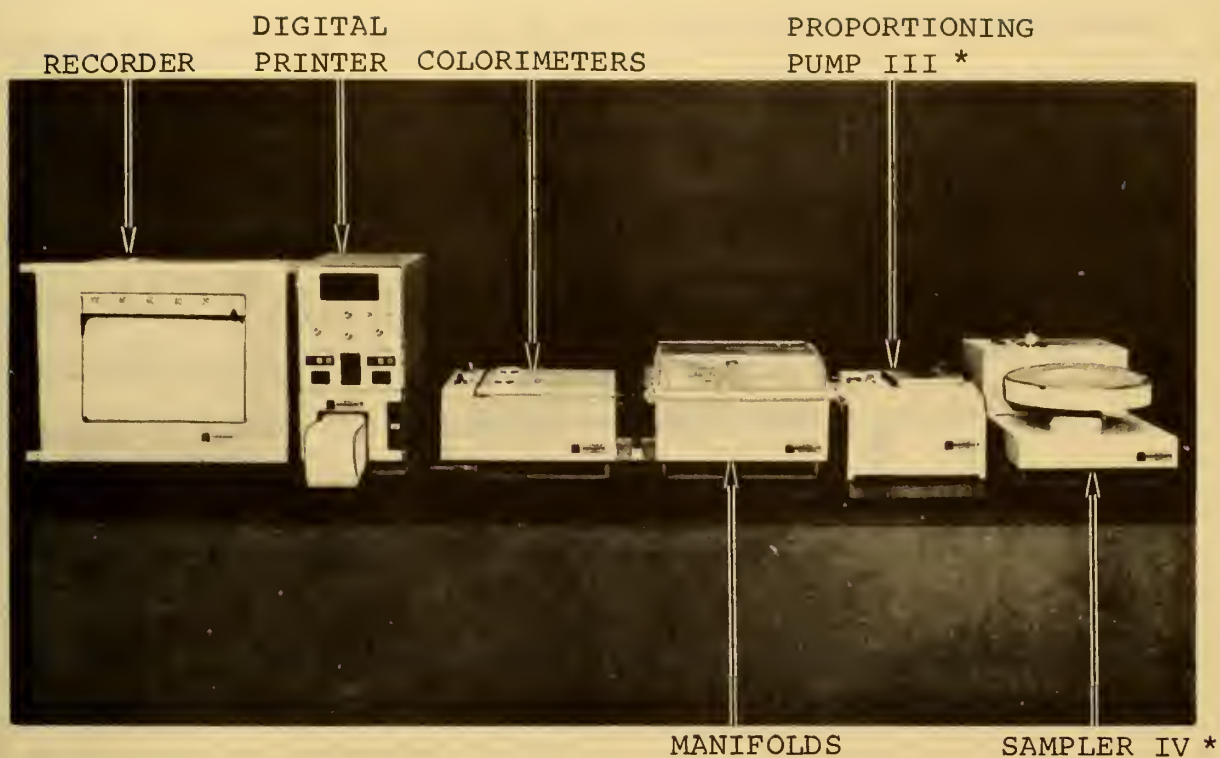
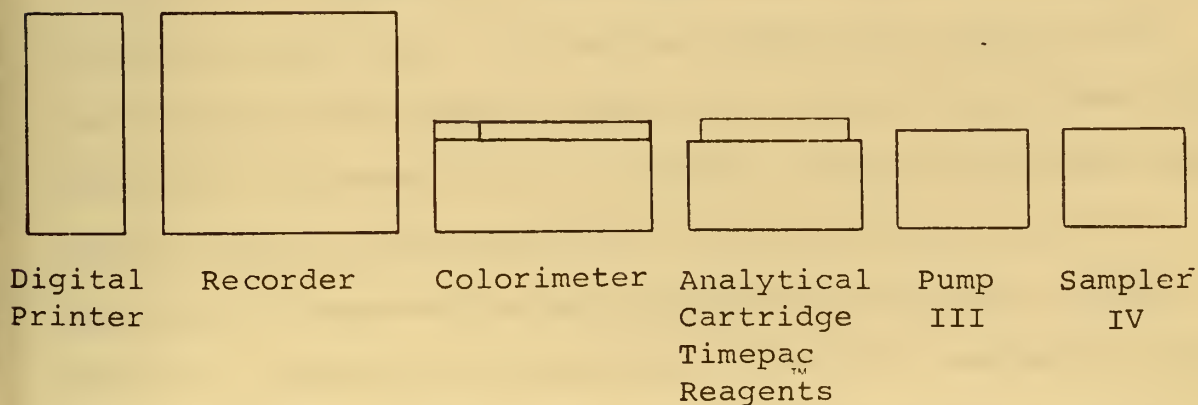


Figure 1. Basic AutoAnalyzer II System (Dual Channel).

*Note: Type Numbers indicate supplier model designations.



the selection of the proper tube diameter. A set of pump tubes was made up and attached to each analytical cartridge so that when a cartridge change was desired the replaced tubes were slipped off and the new set slipped in place. This worked very well and saved the time necessary to attach pump tubes to the cartridges for each change. An air bar is installed on this model which reproducibly allows an air bubble to enter the analytical stream every two seconds. This performed satisfactorily during this study. A single-speed pump was used. A two-speed model is available from Technicon[®] and would save considerable time during the washing phases between cartridge changes when operating continuously for an extended period.

C. ANALYTICAL CARTRIDGES

The analytical cartridges produced by Technicon[®] were used for all nutrient analysis performed. Three cartridges were purchased, one for ORTHO-PHOSPHATE in sea water, one for REACTIVE SILICATE in sea water, and one for NITRATE-NITRITE in sea water. In the cartridges the sample, air, and reagents are properly mixed, the chemical reactions take place and the reaction color develops. These cartridges were compact units, highly portable and sufficiently rigid to withstand transportation and shipboard use without damage. They are, however, not versatile in that all components for a particular procedure are permanently mounted in the cartridge and would be difficult to modify if a different procedure was desired. Two cartridges were normally operated

at one time in dual channel operation. Silicate and nitrate or phosphate and nitrite were normally determined together. This allowed 80 analyses per hour to be performed when the sampler was operating at 40 samples/hour. After about 80 samples were analysed (2 hours), the cartridges were changed and the samples again analysed for the remaining two nutrients. This procedure proved quite satisfactory and an extended period of sampling sea water every 10 minutes could be maintained with a minimum delay before sample analysis. The optimum would obviously be to analyse for all four nutrients at one time but additional equipment would then be necessary.

D. COLORIMETERS

Two Technicon[®] AutoAnalyzer[®] II single-channel colorimeters were used in these continuous flow analytical systems. This model is somewhat different from the older AutoAnalyzer[®] I colorimeter and uses a longer flowcell (five cm vice 1.0 to 1.5 cm). The flow stream from the analytical cartridge enters the colorimeter, is debubbled and then colorimetrically detected at a specified wavelength for the nutrient caused absorbance changes due to nutrient concentration variations. This is accomplished by a dual optical system with two detecting phototubes. This model colorimeter has a log ratio circuit which converts the logarithmic output signal to a linear signal proportional to the nutrient concentration. The standard calibration control allowed the selection of

the desired full scale concentration range during the standardization procedure and was found quite convenient and reproducible. In addition, the adjustment for zero, 100% deflection and baseline (reference) were available and satisfactory. The colorimeters were usually operated without any damping or time averaging circuits used (Normal Mode). At low phosphate levels a two second time averaging mode (Damp 1) was sometimes used if the noise interference was significant. A voltage stabilizer was supplied with each colorimeter. Although some difficulties have been attributed to power fluctuations [Atlas et al. 1971] no problems related to power fluctuations were experienced with this equipment either at sea or in the laboratory.

E. RECORDER

A two-pen BRISTOL RECORDER specified and supplied by Technicon[®] Corporation for the AutoAnalyzer[®] was used.

III. ANALYSES

A. SILICATE ANALYSIS

The automated procedure supplied by Technicon[®], Preliminary Industrial Method No. 186-72W AAII, was followed for reactive silicate analysis with modifications for dual channel operation and standardization procedures. This procedure utilizes ascorbic acid in the reduction of silicomolybdate in acidic solution to molybdenum blue. Oxalic acid is introduced in the flow stream to prevent phosphate interference. The flow diagram for this procedure is shown in Figure 2. As noted in this diagram, the total volume of sample, reagents and air in the Autoanalyzer[®] II (AA II) system is much lower (about 1/3 or less) than in the older system. This results in smaller components, smaller bore tubing and ultimately better performance due to less noise and better mixing conditions. A 5 cm flow cell and 660 nm interference filters were used for this procedure. The sampler was operated at 40 samples/hour with a 4:1 sample-to-wash ratio.

1. Reagents:

AMMONIUM MOLYBDATE: 10 g of reagent-grade ammonium molybdate were dissolved in 1000 ml. of 0.1N sulfuric acid.

OXALIC ACID: 50 g of reagent grade oxalic acid were dissolved in 1000 ml. of double distilled deionized water.

TO SAMPLER IV WASH RECEPTACLE	GRN/GRN(2.00)WATER
20 TURNS 157-0370	BLK/BLK(0.32)AIR
157-B095 20 TURNS	ORN/ORN(0.42)MOLYBDATE
116-0489-01	BLK/BLK(0.32)SAMPLE
BLK/BLK(0.32)OXALIC ACID	
ORN/ORN(0.42)ASCORBIC ACID	
WASTE	GRY/GRY(1.00)FROM F/C

NOTE: FIGURES IN PARENTHESES SIGNIFY FLOWRATE IN ML/MIN

Figure 2. Silicate Method Flow Diagram.

ASCORBIC ACID: 17.6 g of reagent-grade ascorbic acid were dissolved in 500 ml. of double distilled deionized water (DDDW) containing 50 ml. of acetone. This was then diluted to 1000 ml. and 10 drops of Wetting Agent A (available from Technicon®) were added. This reagent was kept refrigerated except when in use and mixed fresh for each cruise.

2. Standards:

STOCK STANDARD A, 10,000 $\mu\text{g/l}$ Si/l: This method of STRICKLAND and PARSONS [1968] was doubled and followed, rather than the referenced Technicon® procedure, in order to minimize the time required for the standard to be in a glass volumetric flask during dissolution. 1.92 g of fine powder sodium silicofluoride were dissolved in a plastic beaker, transferred to a 1000 ml. volumetric flask, and diluted to the mark with DDDW.

STOCK STANDARD B, 1000 $\mu\text{g/l}$ Si/l: 10 ml. of Stock Standard A were diluted to 100 ml. in a volumetric flask and stored in a polyethylene bottle.

WORKING STANDARDS:

<u>ml. Stock B</u>	<u>$\mu\text{g/l}$ Si/l</u>
1.0	10
2.0	20
3.0	30
4.0	40
5.0	50
10.0	100

The required volume of Stock Standard B was pipetted into a 100 ml. volumetric flask and diluted to 100 ml. with DDDW. These standards were prepared fresh at most every 10 hours. During at sea operations only the 30 μ g/l Si/l standard was used to set and check the equipment calibration as the calibration curve proved to be linear (Figure 3). All reagents and standards were mixed in double distilled water which was passed through an ion exchange column just prior to use to minimize silica interference from glass storage vessels. All reagents and standards were stored in polyethylene bottles to prevent additional silica contamination. All glassware, sample cups, and storage bottles were thoroughly washed, rinsed, then rinsed with 1N HCl and finally rinsed three times with DDDW before use.

3. Baseline

The reagent baseline was adjusted to 0% recorder reading with all reagents being introduced into the flow stream and DDDW introduced instead of the sea water sample. This silicate baseline was normally very constant and showed little drift after the system was on line for a short time (about 15 min.). To check the baseline and adjust if necessary, the sampler was stopped in the wash cycle about every 15 minutes for 3 minutes. A baseline adjustment was then made, if necessary, when the recorder reached a steady-state baseline condition. This minimized the baseline correction necessary when correcting data.

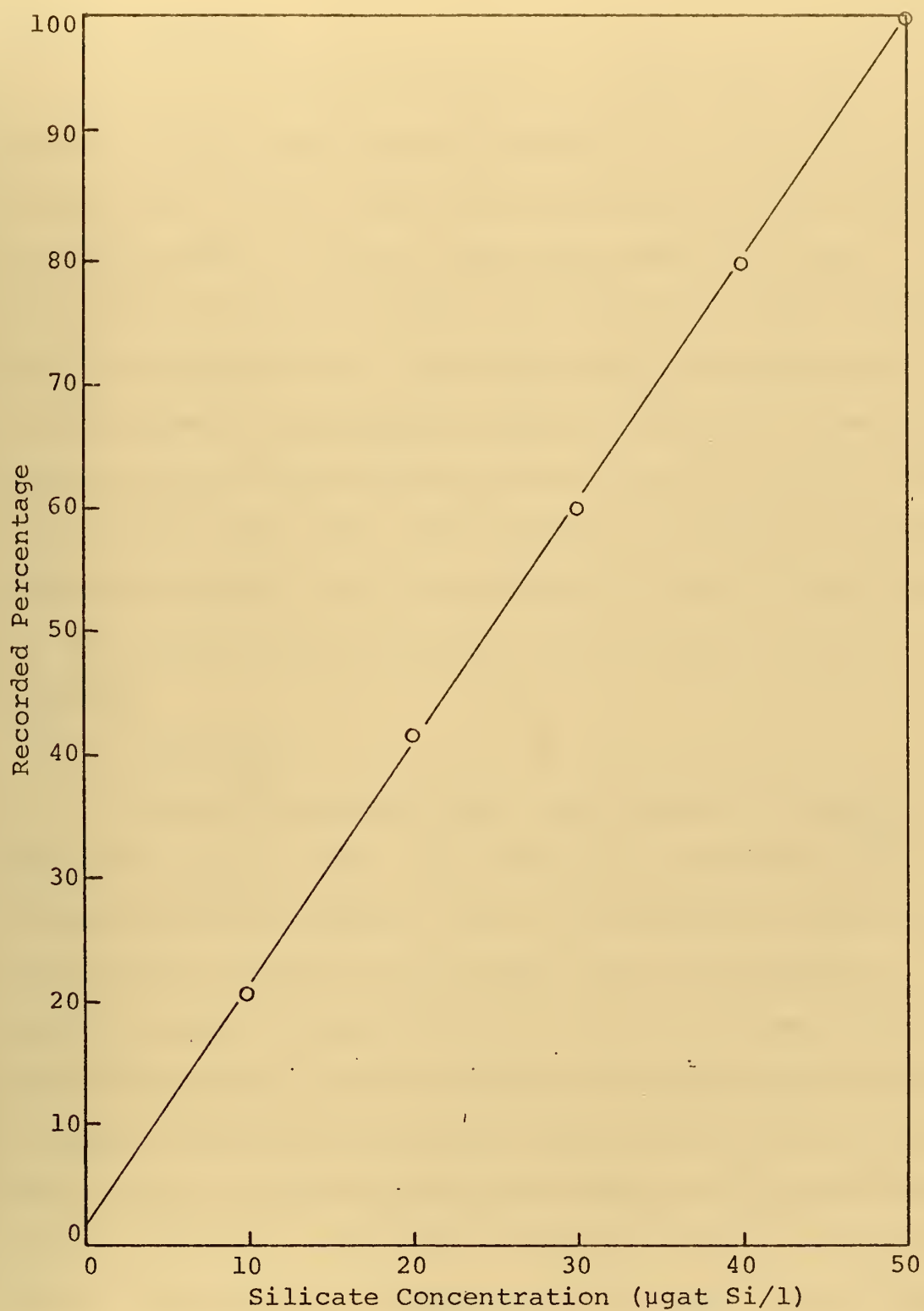


Figure 3. Silicate Linearity Check.

4. Linearity

The silicate procedure was checked twice for linearity using DDDW standards mixed to 10, 20, 30, 40 and 50 $\mu\text{gat Si/l}$. In both runs the results were satisfactory and reproducible. Figure 3 shows the results of one linearity test where recorder percentage is plotted versus standard concentration. Each datum point represents the average value of two standard samples analysed. These tests indicate the maximum deviation from linearity of $\frac{1}{2}\%$ in the range of 0-50 $\mu\text{gat Si/l}$. This range was tested because all sea water analysed during this study was below 50 $\mu\text{gat Si/l}$. For more concentrated sea water further tests will be necessary.

5. Salt Error

All automated procedures [Strickland and Parsons 1968, Atlas et al. 1971, and others] and the Technicon[®] silicate procedure specify that all standards be mixed with low nutrient sea water or synthetic sea water because of the salt effect on the equilibrium of the silicomolybdate reduction reaction. This procedure was undesirable because of apparent optical interference found when synthetic sea water blanks were determined with respect to DDDW baseline without reagents. This effect was also noted by Atlas et al. [1971]. Furthermore, synthetic sea water was found to show significant variation depending on quality of reagents and age of solution. This was also true of sea water obtained at different locations and stored for different periods of

time. Finally, the stability and reproducibility of standards prepared in DDDW was found to be excellent. In order to calibrate with DDDW standards, tests were performed for all analyses to determine the salt error correction necessary.

Silicate standards were prepared in concentrations of 10, 20, 30, and 40 $\mu\text{g/l}$ Si/l in sea water obtained from the area of study (Monterey Bay). A DDDW standard of 30 $\mu\text{g/l}$ Si/l was also prepared for use in calibrating the system before analysing the sea water standards. Three samples of each standard were used for each run performed. Two test runs were performed using DDDW as wash water and baseline. The three sea water standards for each concentration were averaged, then the average recorder value of the silicate concentration in sea water only was subtracted. The results were compared to the DDDW standard calibration curve obtained from the linearity tests. The resulting curves are plotted in Figure 4. Two identical salt effect runs were also performed using sea water only for the wash and baseline [Strickland and Parsons 1968]. The results of the standards were again averaged but no baseline subtraction was necessary. The DDDW standard reference point for the comparison curve was obtained by adding the average recorder percentage value to the sea water silicate value obtained with DDDW baseline. The result of one run is plotted in Figure 5. Both plots gave nearly identical results, as expected, and a near linear salt error of 10% for 100% of tested range is indicated. The combined results were then converted to

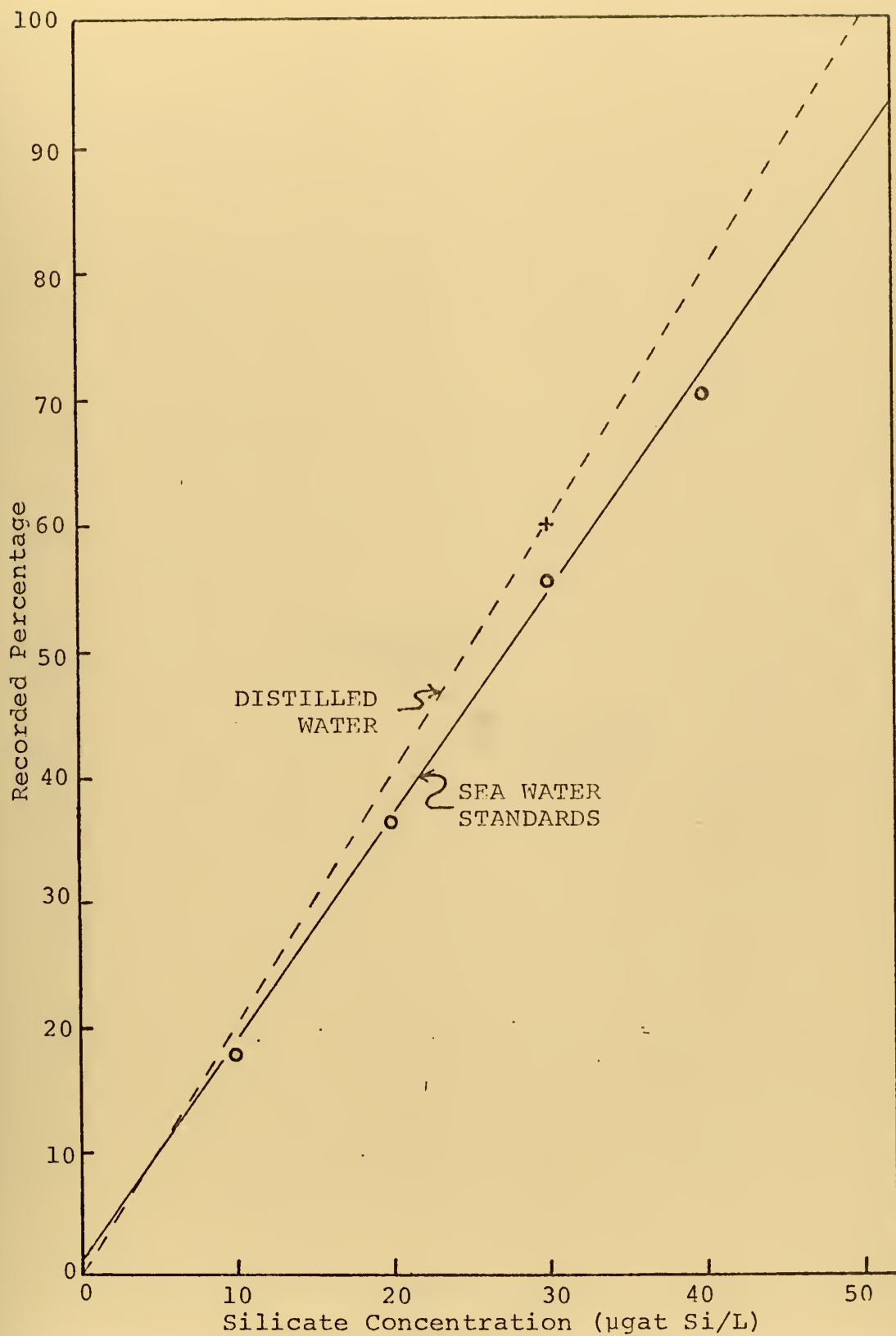


Figure 4. Silicate Salt Error (Distilled Water Wash).

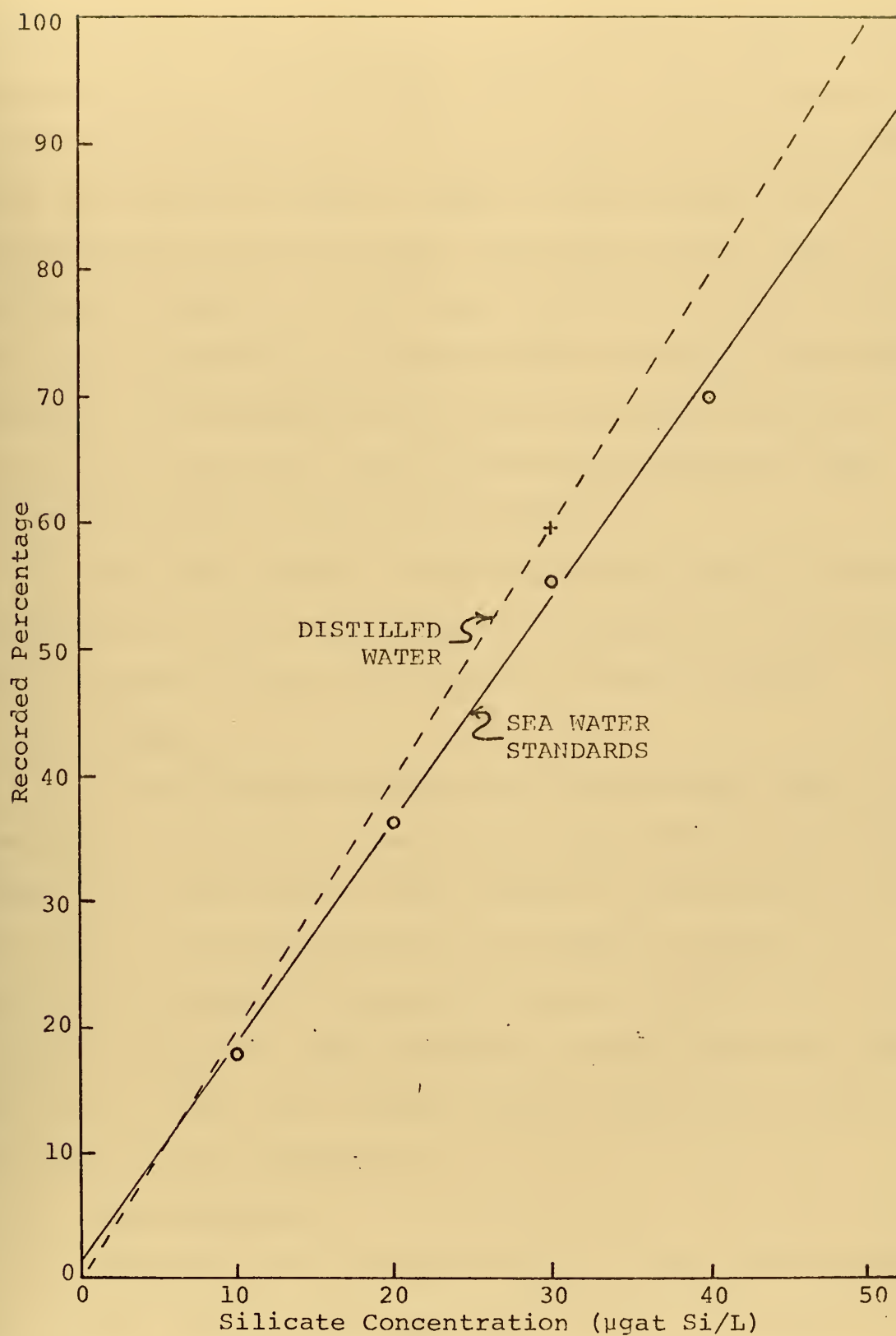


Figure 5. Silicate Salt Error (Sea Water Wash).

concentration values (multiplied by the factor; DDDW Standard Concentration for $\frac{100\% \text{ Recorder Reading}}{100}$). The differences between the concentration values obtained in sea water standards from those obtained in DDDW was then plotted as a concentration correction versus the DDDW standard concentrations in Figure 6. This linear correction curve obtained was used to correct all silicate values obtained using DDDW standards. The maximum error in this procedure should be $\pm 1.5\%$ or $\pm 0.25 \mu\text{g/l Si/l}$ and is considered acceptable when the greater stability of it is considered.

For waters higher in silicate concentration, further investigation should be performed to determine if the range can be extended without significant nonlinear effects.

6. Blanks

A blank determination should be performed daily by sampling the analysed sea water with only DDDW in the reagent lines. This absorbance in the flowcell is believed due to the change in optical density of the higher salinity sea water and is assumed to occur also during analysis with reagents. Silicate blanks determined varied from $0.36 \mu\text{g/l Si/l}$ to $0.46 \mu\text{g/l Si/l}$ with an average value of $0.40 \mu\text{g/l Si/l}$ used in data correction.

7. Data Reduction

Baseline drift was approximately linear [Strickland and Parsons 1968, Atlas et al. 1971] and the resultant correction was added or subtracted from the sample recorder percentage value assuming this linearity between baseline

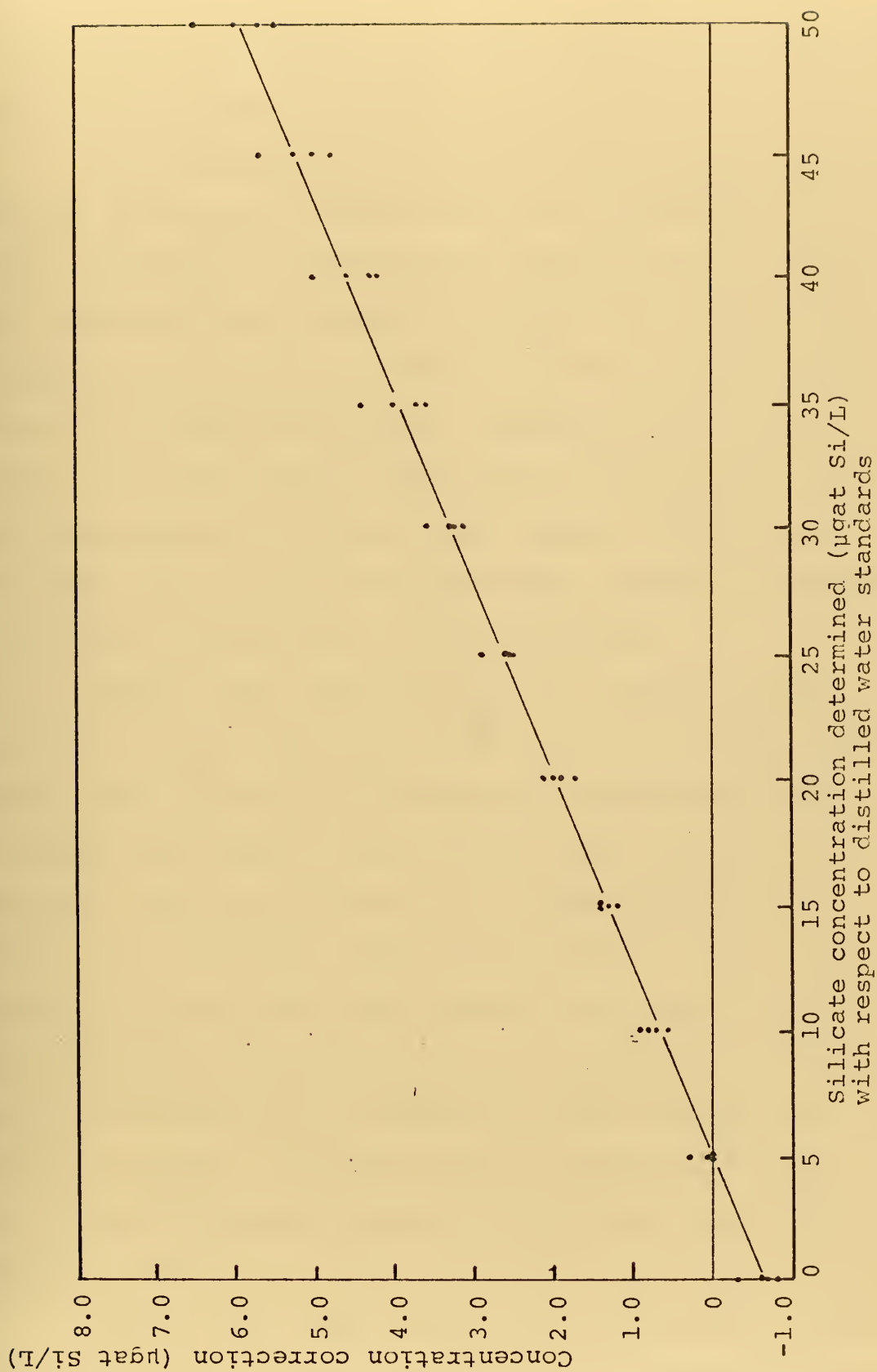


Figure 6. Silicate Salt Error Correction Curve.

checks. When the baseline was checked every 15 minutes this correction was normally very small.

The standardization factor was determined each hour from the calibration standard and used to determine all sample concentrations during the subsequent hour. Consecutive standardization values were compared for significant changes but no attempt was made to correct for variations because of a number of reasons. Linearity could not be assumed. The same change could not be assumed to hold over the entire range of concentrations tested, and the small variation ($\pm 0.5\%$) in standard percentage values was considered to be within the precision of the technique.

Samples were identified on the recorder and the percentage of full scale was logged using the highest value of the peak nearest the trailing edge (closest to the end of sample when steady state or near steady state was obtained). This is indicated in a representative plot (Figure 7). Percentage values can be read to 0.1%. The baseline correction was then applied, the blank correction subtracted and the concentration with respect to DDDW standard was determined by multiplying by the concentration conversion factor. Finally, the salt error correction was applied as discussed above and the final corrected concentration obtained.

During this study all data reductions were performed manually but for a larger volume of data a computer program would be desirable [Atlas et al. 1971].

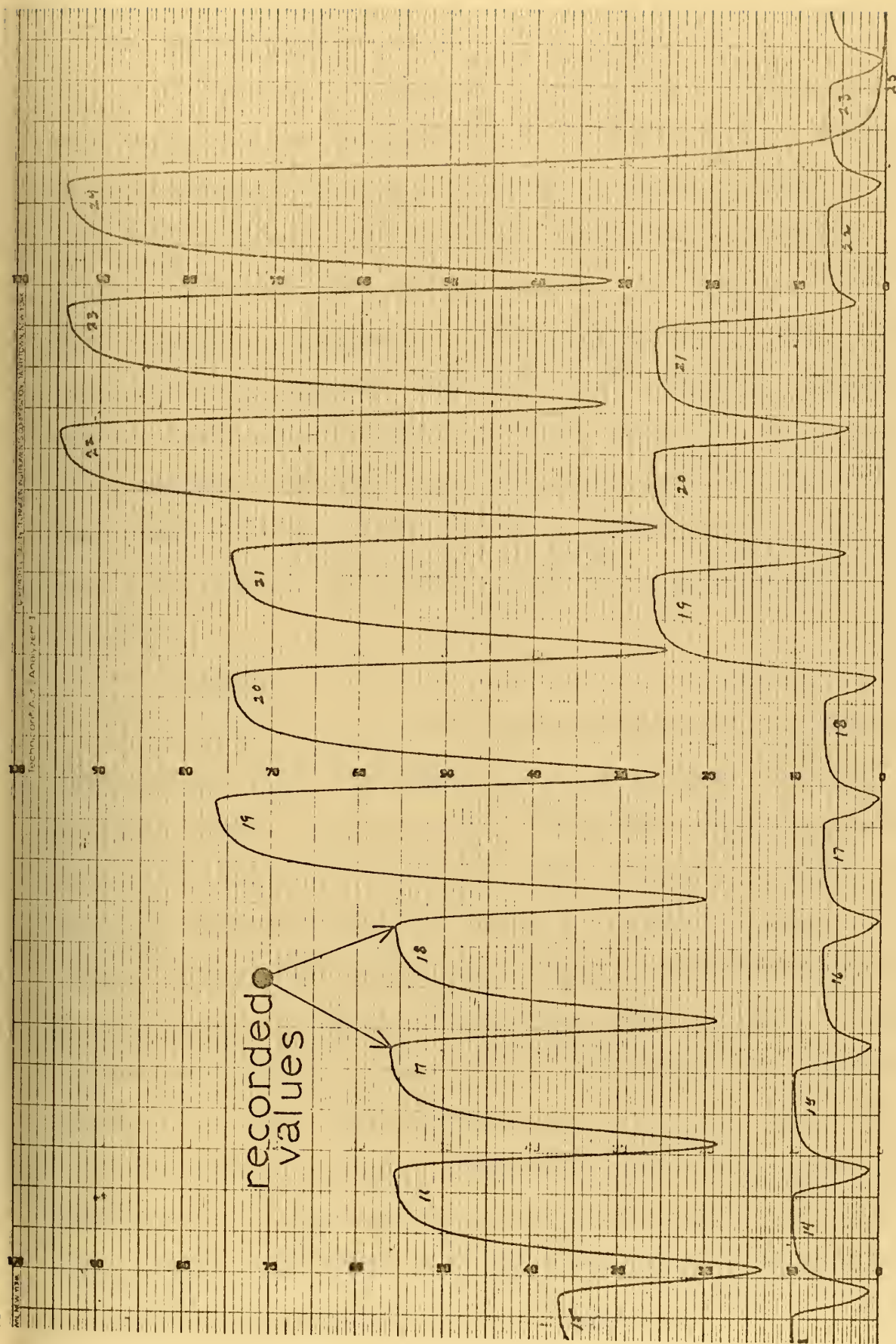


Figure 7. Dual Channel Operation Recorder Output.

8. Interference

No specific interference tests were conducted during this study, however phosphate and nitrate standards analysed in dual operation with this silicate procedure showed no significant effect. This confirms the results of Atlas et al. [1971] who used the AAI system. Atlas et al [1971] also reported no noticeable arsenic interference (to 0.8 μg at Ar/l) in their studies. The Technicon[®] procedure indicates tannin, large amounts of iron, color, turbidity and sulfide may interfere with this procedure. All samples obtained in this study were analysed directly without filtration and gave good results with little or no noise attributed to turbidity.

9. Summary

Extreme care must be used to prevent silica contamination from glass containers for this analysis. Careful analysis during linearity tests indicated a silicate increase of 2 - 5% (1.0 - 2.5 μg at Si/l) when standards remained in glass volumetric flasks for only 10-30 minutes. Also, synthetic sea water stored in a brown glass bottle indicated a 25.0 μg at Si/l increase during one month storage. During cruise four analyses (see below), approximately 10 samples taken in nutrient deficient open sea water gave negative 2% (-1.0 μg at Si/l) results. These results below baseline indicate a 1.0 μg at Si/l contamination level in the DDDW wash and/or reagents used during this cruise. The absolute silicate concentration values are therefore probably low by

1.0 $\mu\text{g/L}$ Si/l for this cruise and are indicated as errors below. The relative values of concentration variations are believed to be much better. Strickland and Parsons [1968] note that synthetic sea water used for standard preparation should be below 1 or 2 $\mu\text{g/L}$ Si/l. This is the range of contamination found to exist during cruise four. Additional tests in the laboratory and a review of other cruise data indicate the normal contamination level is significantly lower if the above precautions are followed.

The silicate procedure was found quite stable with little noise interference from bubble patterns or optical density changes. The peak plateaus were very good at 40 samples/hour. Proper wash procedures must be followed and sufficient time for baseline stabilization allowed prior to commencing analysis (at least 15 min.) in order to minimize baseline drift during analysis. By checking the baseline every 15 minutes during analysis, baseline corrections normally can be reduced to below 1%. Hourly standardization gave good results and corrected for significant temperature changes or reagent deterioration experienced.

Table I gives a summary of errors determined for the silicate procedure during both laboratory and shipboard operation for 0-50 $\mu\text{g/L}$ Si/l range of calibration. Error data from Atlas et al [1971] (AA-I procedure) is also presented for comparison purposes. With additional experience using this equipment and refinement of techniques these errors probably can be reduced.

TABLE I

SOURCES AND MAGNITUDE OF ERRORS ($\mu\text{gat Si/l}$)
IN THE CONCENTRATION RANGE OF 0-50 $\mu\text{gat Si/l}$

	AA-II (Note 2)	Atlas et al. (AA-I) (Note 2)
Recorder Reading Error	± 0.05	± 0.15
Precision (2σ)	± 0.049 (Note 1)	± 0.06
Salt Effect	± 0.250	---*
Salt Error	---*	$-.045 \pm .004/1\%$ increase in salinity
Non-linearity Error	± 0.250	± 0.25 (est.)
Minimum Detection Limit	0.5 $\mu\text{gat Si/l}$ above baseline	---**
Contamination Level Error	$\pm 1.0 \mu\text{gat Si/l}$	---**
Maximum Total Relative Error	$\pm 0.55 \mu\text{gat Si/l}$	---**
Est. Maximum Absolute Error	$1.0 \pm 0.55 \mu\text{gat Si/l}$	---**

Note 1: Calculated from results of 32 triplicate standards.

Note 2: AA-I (AutoAnalyzer[®] I); AA-II (AutoAnalyzer[®] II).

* AA-I procedure used standardization in artificial seawater and defined salt error differently.

** Not specified.

B. ORTHO PHOSPHATE ANALYSIS

Technicon[®] Industrial Method No. 155-71W was followed for phosphate analysis as modified for dual channel operation. In this automated procedure ortho phosphate is colorimetrically determined as the phosphomolybdenum blue complex at 880 nm [Murphy and Riley 1962]. The flow diagram for this procedure is shown in Figure 8. A single reagent solution is used consisting of an acidified solution of ammonium molybdate containing ascorbic acid and a small amount of antimony. A heating bath of 37.5°C provides for temperature stability and time regulation of the chemical reaction. Silicon (Si) phototubes are used for improved sensitivity while using 880 nm interference filters. The sampling rate was modified to 40 samples/hour at a 4:1 sample-to-wash ratio for compatible dual channel operation. All sea water analysed was within the specified range of 0-4 µgat P/l.

1. Reagents

SULFURIC ACID: 136 ml. of concentrated sulfuric acid were added to 800 ml of DDDW while cooling. The cooled solution was diluted to 1000 ml.

AMMONIUM MOLYBDATE: 40 g of reagent-grade ammonium molybdate were dissolved in 800 ml of DDDW, then diluted to 1000 ml.

ASCORBIC ACID: 18 g of reagent-grade ascorbic acid were dissolved in 800 ml of DDDW, then diluted to 1000 ml. This reagent was refrigerated when not in use.

(Range: 0-4 "gat P/1)

MANIFOLD NO. - 116-D221-01

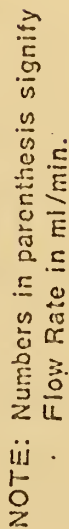


Figure 8. Ortho Phosphate Method Flow Diagram.

ANTIMONY POTASSIUM TARTRATE: 3.0 g of reagent-grade antimony potassium tartrate were dissolved in 800 ml of DDDW, then diluted to 1000 ml.

COMBINED WORKING REAGENT: The combined color reagent (Figure 8) was prepared by mixing the above reagents in order; 50 ml sulfuric acid, 15 ml of ammonium molybdate, 30 ml of ascorbic acid, and 5 ml of antimony potassium tartrate. This reagent was mixed well and used from a brown reagent bottle to reduce deterioration. A new solution was mixed every 8 hours or when significant discoloration developed.

WATER DILUENT: 10 drops of Wetting Agent A were added to 1000 ml of DDDW. This solution assisted in producing good bubble patterns. It must not be used for wash water or rinse due to possible resulting contamination.

2. Standards

STOCK STANDARD A, 1000 μ gat P/l: 0.136 g of anhydrous potassium dihydrogen phosphate was dissolved in 500 ml of DDDW and diluted to 1000 ml in a volumetric flask. 1 ml of chloroform was added as a preservative.

STOCK STANDARD B, 40 μ gat P/l: 10 ml of Stock Standard A were diluted to 100 ml with DDDW in a volumetric flask. This standard was prepared fresh daily.

WORKING STANDARDS:

<u>ml Stock B</u>	<u>µgat P/l</u>
0.20	0.08
2.0	0.8
4.0	1.6
6.0	2.4
8.0	3.2
10.0	4.0

The required volume of Stock Standard B was pipetted into a 100 ml volumetric flask and diluted to 100 ml with DDDW. These standards were prepared fresh daily. During at sea operations only the 2.4 µgat P/l standard was used to set and check the equipment calibration as the calibration curve proved to be linear (Figure 9). All glassware, sample cups, and storage bottles were thoroughly washed, rinsed, then rinsed with 1N HCl and finally rinsed three times with DDDW before use.

3. Baseline

The phosphate baseline adjustment was similar to the silicate procedure. This procedure, however, being of much lower concentration range was more subject to baseline fluctuations and noise. Contamination of wash water is extremely easy and all foreign material, dust, etc. must be guarded against. Contamination of wash or reagents is indicated by an erratic baseline condition. Bubble noise was sometimes a problem with this procedure and Damp 1

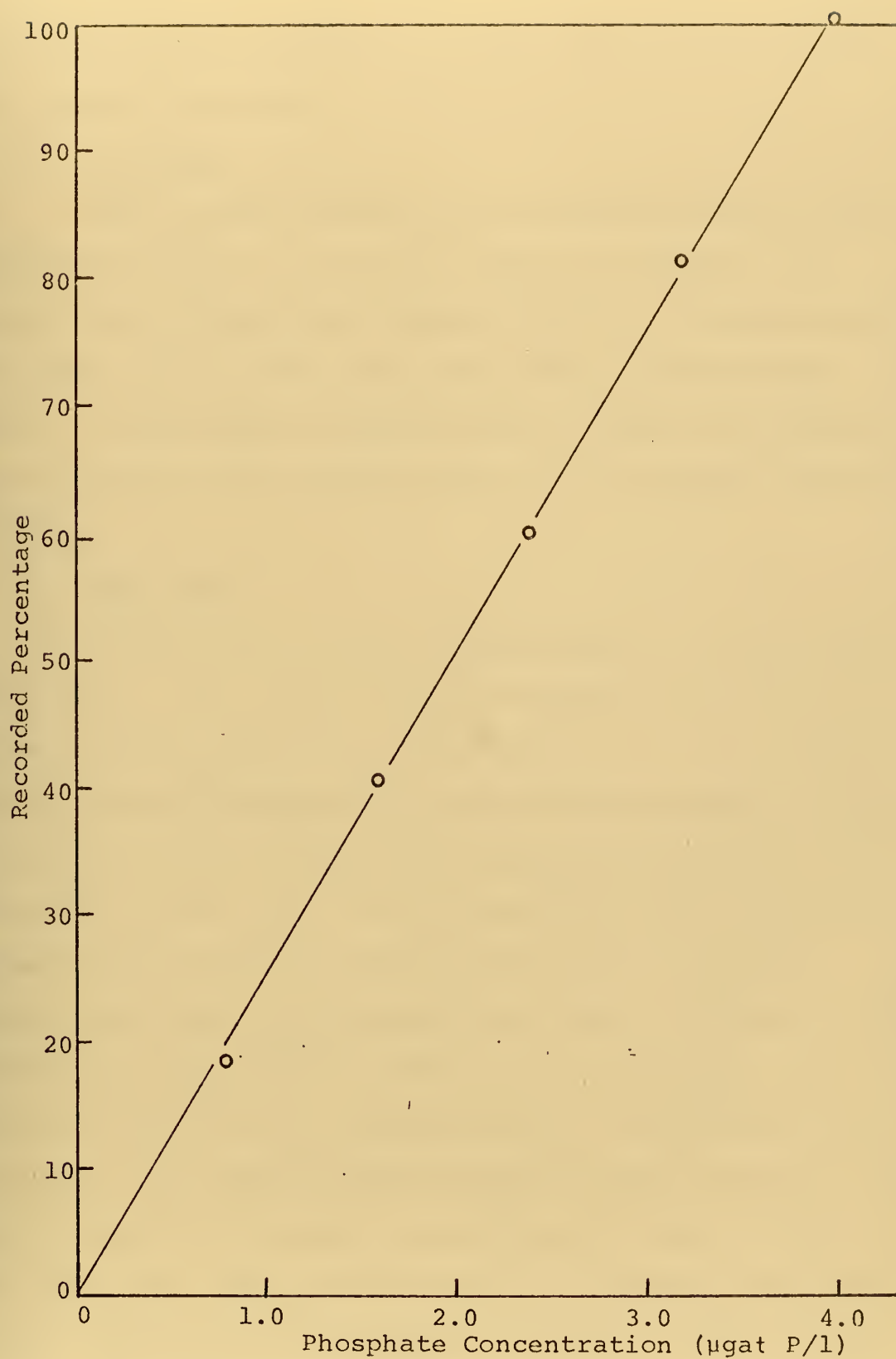


Figure 9. Phosphate Linearity Check.

operation of the colorimeter (as specified by Technicon[®]) was sometimes necessary.

4. Linearity

Four linearity test runs were performed using DDDW standards of 0.8, 1.6, 2.4, 3.2, and 4.0 $\mu\text{gat P/l}$. All results were satisfactory and reproducible. The linearity was within $\pm 0.7\%$ (0.028 $\mu\text{gat P/l}$) over the range tested. Figure 9 illustrates a typical result. Again, each datum point represents the average value of two standard samples analysed.

5. Salt Error

Although past authors [Strickland and Parsons 1968, Atlas et al. 1971] using similar procedures with the AA-I system indicate there is a significant salt error involved and specify standardization in artificial sea water or low nutrient sea water, Technicon's procedure indicates a salt error of less than 1%. Two salt error test runs were performed comparing DDDW standard results with standards mixed in sea water. The results are shown in Figure 10 and confirm the Technicon[®] procedure showing a maximum salt error of 1% at very low concentrations. A single test run for salt error comparing DDDW standards with artificial sea water standards indicated a possible salt effect of 10% (0.4 $\mu\text{gat P/l}$). This may explain the reported errors but further tests would be necessary to confirm these results.

6. Blanks

Blank determinations were performed similar to those discussed for silicate. The results, however, were much more significant and indicated an average of 4.48% (.18 μ gat P/l) optical density blank correction was necessary for the phosphate determinations. Further tests in the laboratory confirmed this value. The average artificial sea water blank, determined for a check, was 4.35%, in good agreement with the subject sea water results.

7. Data Reduction

Data reduction of the phosphate analysis was like that of silicate except no salt error corrections were necessary.

8. Interference

Although no specific tests were performed, no significant interference was noted during dual operation by either silicate or nitrate standards prepared in DDDW. Artificial sea water standards gave varying interference results from a low of 4% to a high of 21%! This was a major concern when operating dual with nitrate-nitrite or silicate standards prepared in artificial sea water and resulted in the salt effect experimentation. As noted above, this procedure is measuring a very low concentration and subject to contamination and noise when in the lower end of the range.

Arsenate interference [Johnson 1971, Atlas et al. 1971] is expected if the phosphate is low level and arsenate concentration abnormally high.

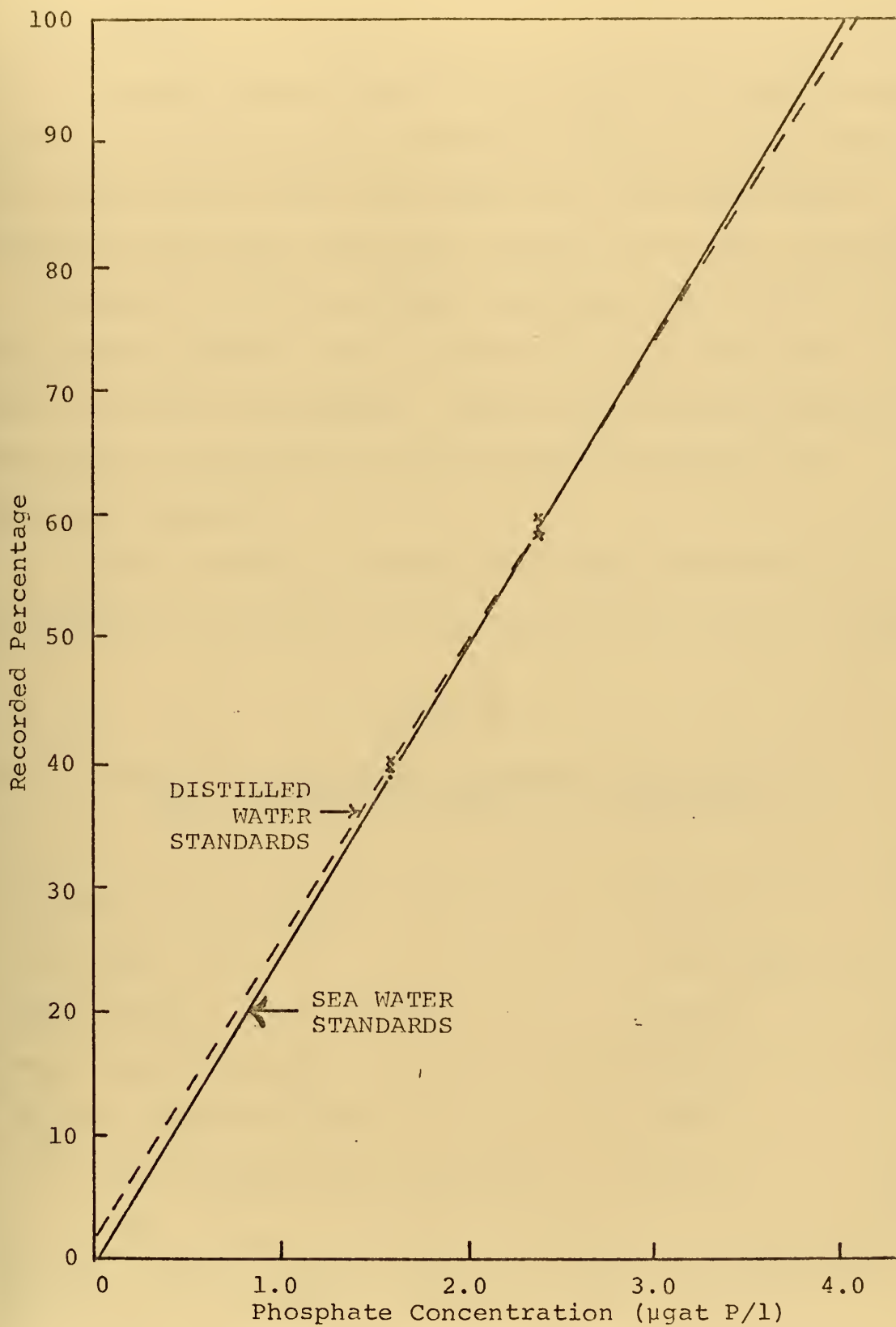


Figure 10. Phosphate Salt Error Test.

9. Summary

Although greater difficulties with blank corrections, baseline stability, and contamination problems were found with this procedure than the others used, the techniques adopted and discussed above were reliable and very sensitive.

Here, as in the silicate technique, the baseline, after proper washout, must be allowed to stabilize well before analysis is attempted. Baseline and standardization procedures as discussed for the silicate procedure are considered necessary.

Table II gives a summary of errors determined for the phosphate procedure for the range of 0-4 μg at P/l tested.

TABLE II

SOURCES AND MAGNITUDE OF ERRORS (μg at P/l) IN
THE CONCENTRATION RANGE OF 0-4 μg at P/l

Recorder Reading Error	± 0.004
Precision (2σ)	± 0.037 (Note 1)
Salt Effect	± 0.020
Non-linearity Error	± 0.028
Minimum Detection Limit	$\pm 0.04^*$
Calculated Maximum Absolute Error	± 0.089

* Technicon® procedure indicates 0.08 μg at P/l as minimum detection limit. Results indicate better performance providing all errors indicated above are not maximum and cumulative.

Note 1: Calculated from results of 33 duplicate standards.

C. NITRATE-NITRITE ANALYSIS

Technicon[®] Industrial Method No. 158-71W was followed for the nitrate and nitrite analysis. This procedure was modified to extend the concentration range to 25 µgat N/l and change the standardization procedure.

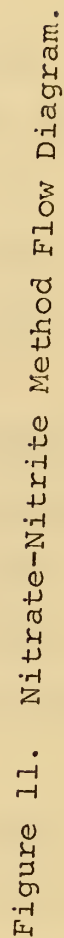
The flow diagram for this procedure is given in Figure 11. Determination of nitrate is accomplished by first reducing the nitrate to nitrite in a 14 inch reductor tube filled with copper-cadmium [Armstrong et al. 1967, Grasshoff 1969]. The nitrite ion then reacts with acidified sulfanilamide to form a diazo compound. This compound couples with N-1-naphthylethylene-diamine dihydrochloride to form a purple azo dye. The color produced is colorimetrically determined at 550 nm. A sampling rate of 40 samples/hour and a 4:1 sample-to-wash ratio was used. When analysing using the reduction column the resultant value represented total nitrate plus nitrite concentrations. Nitrite alone was determined by removing the reduction column. The nitrate concentration value was then determined by difference. This method was normally calibrated for the range of 0-25 µgat N/l instead of the specified range of 0-5 µgat N/l.

1. Reagents

AMMONIUM CHLORIDE: 10 g of reagent-grade ammonium chloride were dissolved in DDDW (made basic to PH 8.5 with ammonium hydroxide) and diluted to 1000 ml.

COLOR REAGENT: 200 ml of concentrated phosphoric acid were added to 1500 ml of DDDW. 20 g of reagent-grade

1894. 1895.



sulfanilamide were then added and dissolved (solution heated). One gram of reagent-grade N-1-naphthylethylene-diamine dihydrochloride was added and dissolved. The solution was diluted to two liters with DDDW and 20 drops of Brij-35 wetting agent (available from Technicon[®]) added. This solution was stored in polyethylene bottles and refrigerated when not in use.

CADMIUM COLUMN: 10 g coarse cadmium powder (purchased from Technicon[®]) was rinsed well with one Normal HCl solution and then with DDDW to remove any grease and dirt. The cadmium powder was then treated with 50 ml of two percent copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) solution. The Cd powder was stirred well in this solution until brownish semi-colloidal copper particles formed in the liquid. The supernatant liquid was decanted and the powder thoroughly washed with DDDW until no copper particles remained in the clear water (10 to 15 washings). It is very important to remove all colloidal materials which would restrict flow and carry-over into the tubing and flowcell.

A glass U-tube (0.081 inch I.D.) was used for the column. This tube performed satisfactorily but was difficult to fill and empty. To fill the column the tube was submerged under water and all air allowed to escape. The treated cadmium powder, still in the final wash water, was sucked into a long glass dropper, the tip of which had been cut so the powder could pass. The dropper was then submerged above the tube and the cadmium water mixture discharged into the

tube. Care was taken to prevent any bubbles from entering the tube. During filling, the column was gently tapped to insure proper packing. When the column was nearly filled (about $\frac{1}{4}$ inch from the ends) glass wool was inserted to prevent the cadmium from dropping out. After starting the pump to remove air from the analytical stream, the column was inserted as indicated in the flow diagram.

The reductor column was activated by sampling Stock Standard B (see below) solution for five minutes, followed by a $\frac{1}{2}$ hour wash with DDDW. Columns prepared in this manner with fresh cadmium performed well for over 500 samples.

2. Standards

STOCK STANDARD A, 1000 $\mu\text{g/l}$: 0.101 g of potassium nitrate was dissolved in DDDW and diluted to 1000 ml. One ml of chloroform was added as a preservative. This standard was stored in a brown glass bottle.

STOCK STANDARD B, 50 $\mu\text{g/l}$: Five ml of Stock Standard A were diluted to 100 ml in a volumetric flask. This standard was prepared each time Working Standards were required.

WORKING STANDARDS

<u>ml Stock B</u>	<u>µgat N/l</u>
0.20	0.1
2.0	1.0
4.0	2.0
6.0	3.0
8.0	4.0
10.0	5.0
20.0	10.0
40.0	20.0

The required volume of Stock Standard B was pipetted into a 100 ml volumetric flask and diluted to 100 ml with DDDW.

These standards were prepared fresh daily. During at sea operations usually either the 10.0 µgat N/l or 20.0 µgat N/l, depending on the range desired, standard was prepared to set and check the equipment calibration as the calibration curve proved to be linear (Figure 12). All glassware, sample cups, and storage bottles were thoroughly washed, rinsed, then rinsed with one Normal HCl and finally rinsed three times with DDDW before use.

3. Baseline

The nitrate and nitrite baseline adjustment was identical to the silicate procedure. This procedure proved to be the most stable of those used and very little baseline drift was noted after the system had stabilized. It was not uncommon to have zero baseline correction during a two hour run.

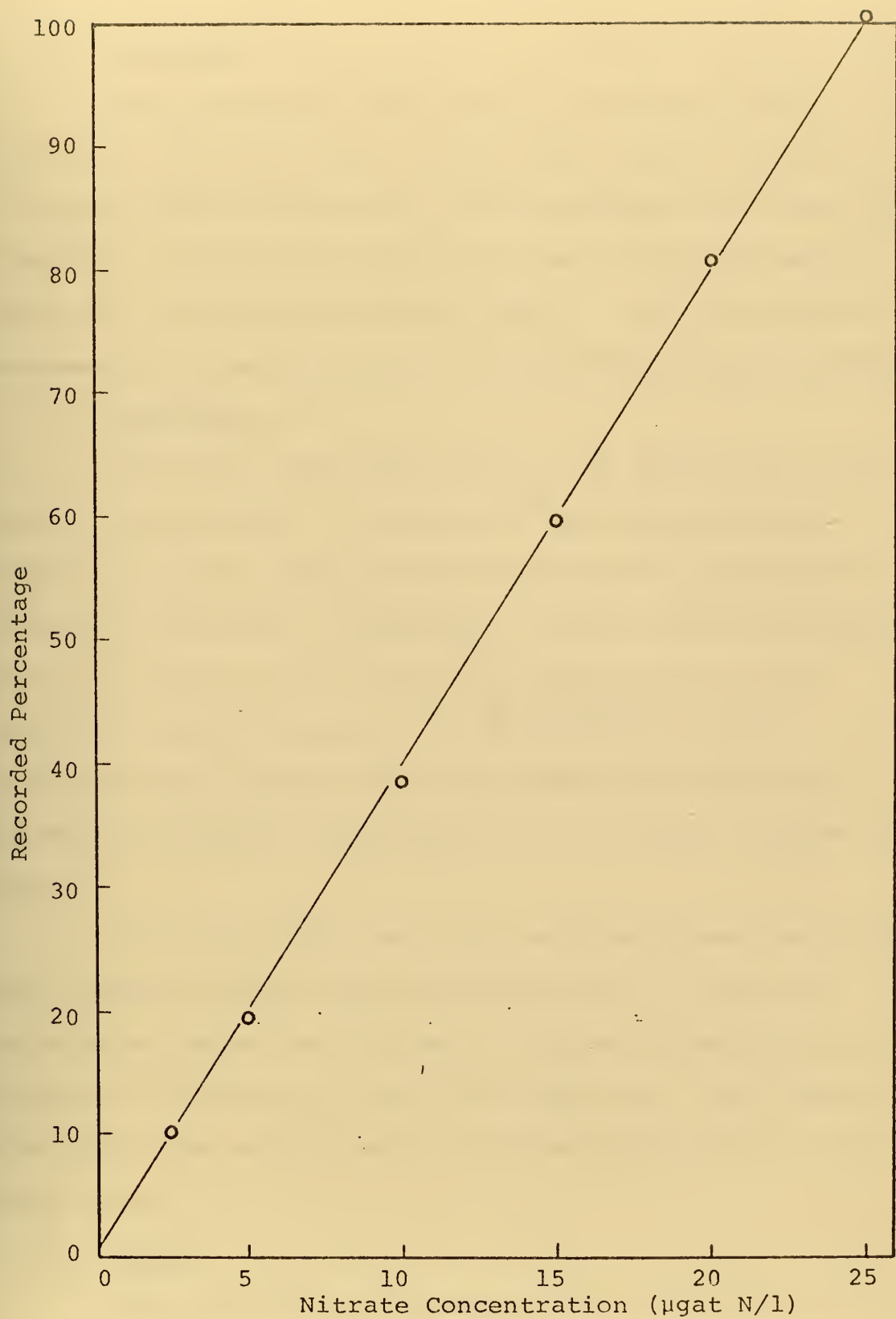


Figure 12. Nitrate Linearity Check.

4. Linearity

Three linearity test runs were performed using DDDW standards of 2.5, 5.0, 10.0, 15.0, 20.0, and 25.0 $\mu\text{gat N/l}$. All results were satisfactory and reproducible and indicated linearity of $\pm 1.0\%$ (0.25 $\mu\text{gat N/l}$) over the range tested. Figure 12 illustrates a typical result. Each datum point represents the average value of two standard samples analysed.

5. Salt Error

Here again, published data is not consistent on the degree of salt effect. Technicon's[®] procedure indicated slight salt effect and specified standards be prepared in artificial sea water. Atlas et al. [1971] indicated negligible salt effect in the range 0-40 $\mu\text{gat N/l}$ but still specified standards prepared in artificial sea water. Strickland and Parsons [1968] indicated salt effects and recommended standards be prepared in low nitrate surface sea water.

Four salt effect test runs were performed comparing DDDW standard results with standards mixed in sea water. One representative run is shown in Figure 13 and indicates a maximum difference of 0.6% (0.15 $\mu\text{gat N/l}$). All results were comparable and indicate an insignificant error in the tested range.

6. Blanks

Blank determinations were performed similar to those for silicate. Average values for blanks obtained were: Nitrate 0.40% (0.1 $\mu\text{gat N/l}$), Nitrite 0.38% (0.095 $\mu\text{gat N/l}$).

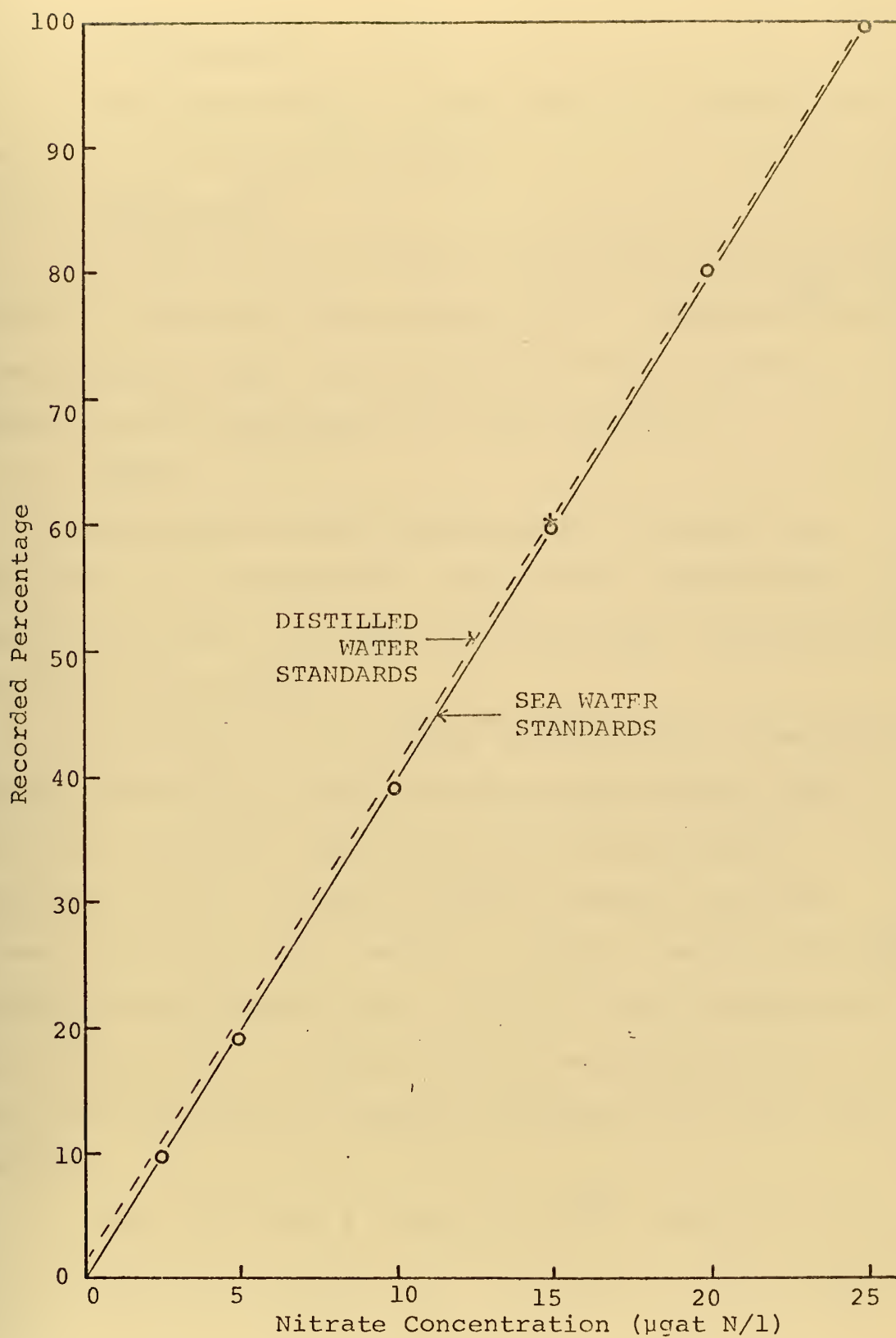


Figure 13. Nitrate Salt Error Test.

7. Data Reduction

Data reduction for nitrate and nitrite analysis was the same as for phosphate analysis.

8. Interference

No significant interference was noted from phosphate or silicate standards when operating dual. Technicon[®] indicates abnormally high concentrations of metal ions may produce positive interference on this analysis.

9. Summary

This procedure for nitrate-nitrite analysis was very stable and reproducible. Very little recalibration or baseline adjustment was necessary after proper stabilization and initial adjustment.

The Cadmium column proved to be the most troublesome element [Atlas et al. 1971, Strickland and Parsons 1968]. One column, prepared from reactivated cadmium powder, apparently not well cleaned, rapidly clogged causing upstream back pressure and leakage. Proper cleaning and copper treatment should prevent this. Care in column preparation and exclusion of air resulted in good performance and no significant decrease in reduction efficiency for over 500 analyses.

Table III gives a summary of errors determined for the nitrate-nitrite analysis for the range of 0-25 µgat N/l tested.

TABLE III

SOURCES AND MAGNITUDE OF ERRORS ($\mu\text{gat N/l}$)
FOR CONCENTRATION RANGE OF 0-25 $\mu\text{gat N/l}$

Recorder Reading Error	± 0.025
Precision (2σ)	± 0.107 (ave of 23 triplicate samples)
Salt Effect	± 0.075
Non-Linearity Error	± 0.250
Minimum Detection Limit	0.100
Calculated Maximum Absolute Error	± 0.457

Although the precision determined from laboratory tests of this procedure is quite good (less than 0.5%) compared to earlier results [Atlas et al. 1971] of $\pm 2\%$, the maximum absolute error becomes significant when analysing low nitrate-nitrite concentration waters. This problem was partially corrected by recalibrating the system for a lower concentration range when low nitrate waters were experienced. The nitrite concentrations generally did not vary significantly with changing nitrate values and all nitrite concentrations obtained in this study were below 1.0 $\mu\text{gat N/l}$. The nitrite analysis was not calibrated with nitrite standards but used the nitrate standards prior to removal of the cadmium column and checked after the column was reinstalled following a run (about 2 hours). This appeared to be satisfactory and no significant calibration change was noted

during this period. A serious deficiency in technique resulted from not reducing full scale range down to 0-5 $\mu\text{g/L}$ or less when preparing for nitrite analysis but continuing to operate at the previous nitrate range (0-25 $\mu\text{g/L}$ or 0-10 $\mu\text{g/L}$). Consequently, the values obtained for nitrite concentrations are subject to rather large relative errors (approaching the values of the determined concentrations) and must be considered only approximate. In further study the equipment must be calibrated for the range of concentrations determined to minimize the errors found in the higher ranges.

IV. SHIPBOARD OPERATION

To enable near real-time analysis and prevent the necessity of freezing samples with the subsequent changes of nutrient concentration resulting from storage, time, handling, etc., the AutoAnalyzer[®] was operated at sea.

A. EQUIPMENT PREPARATION

The AA-II system was prepared for shipboard use by installing the components in three heavy plywood cases (Figure 14). The first case contained the sampler and pump. The second case contained the three reagent cartridges, two colorimeters and associated voltage stabilizers. The third case housed the recorder (Figure 15). The components were secured to the bottom of the case using nylon securing straps. Foam rubber padding was under and around the sides of all components to prevent shock damage. During transportation the components were further padded above with foam rubber and the case covers securely attached. Reagent bottles were held in circular wells cut into a false bottom built 1½" above the actual bottom. This arrangement prevented sliding motion of the bottles and components during heavy seas even if the retaining straps were removed for short periods. The cases were placed together as seen in Figure 14 with the sampler located near a sink and firmly secured to the bench. Half the hold down straps were

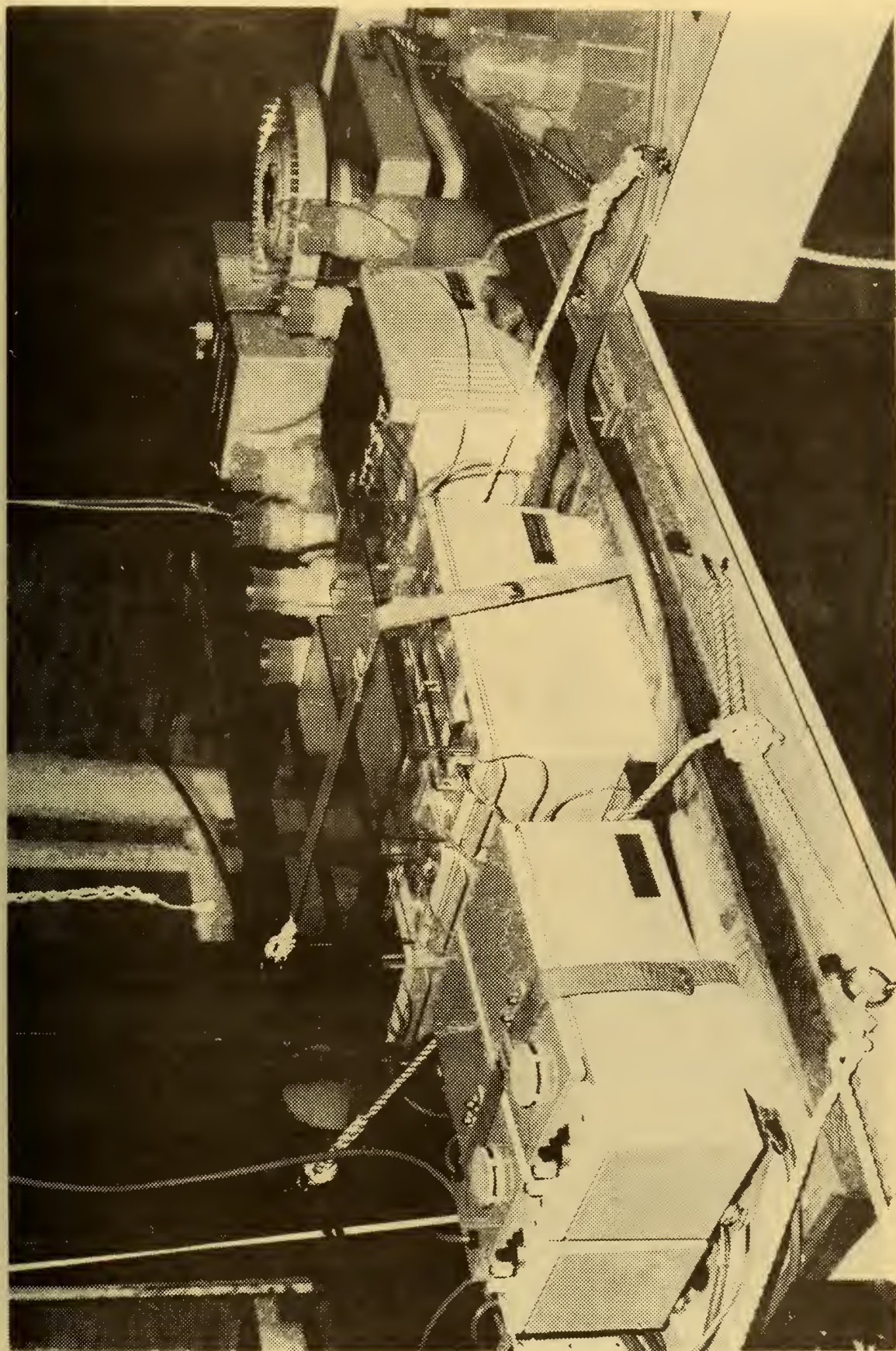


Figure 14. Shipboard Arrangement of Components.

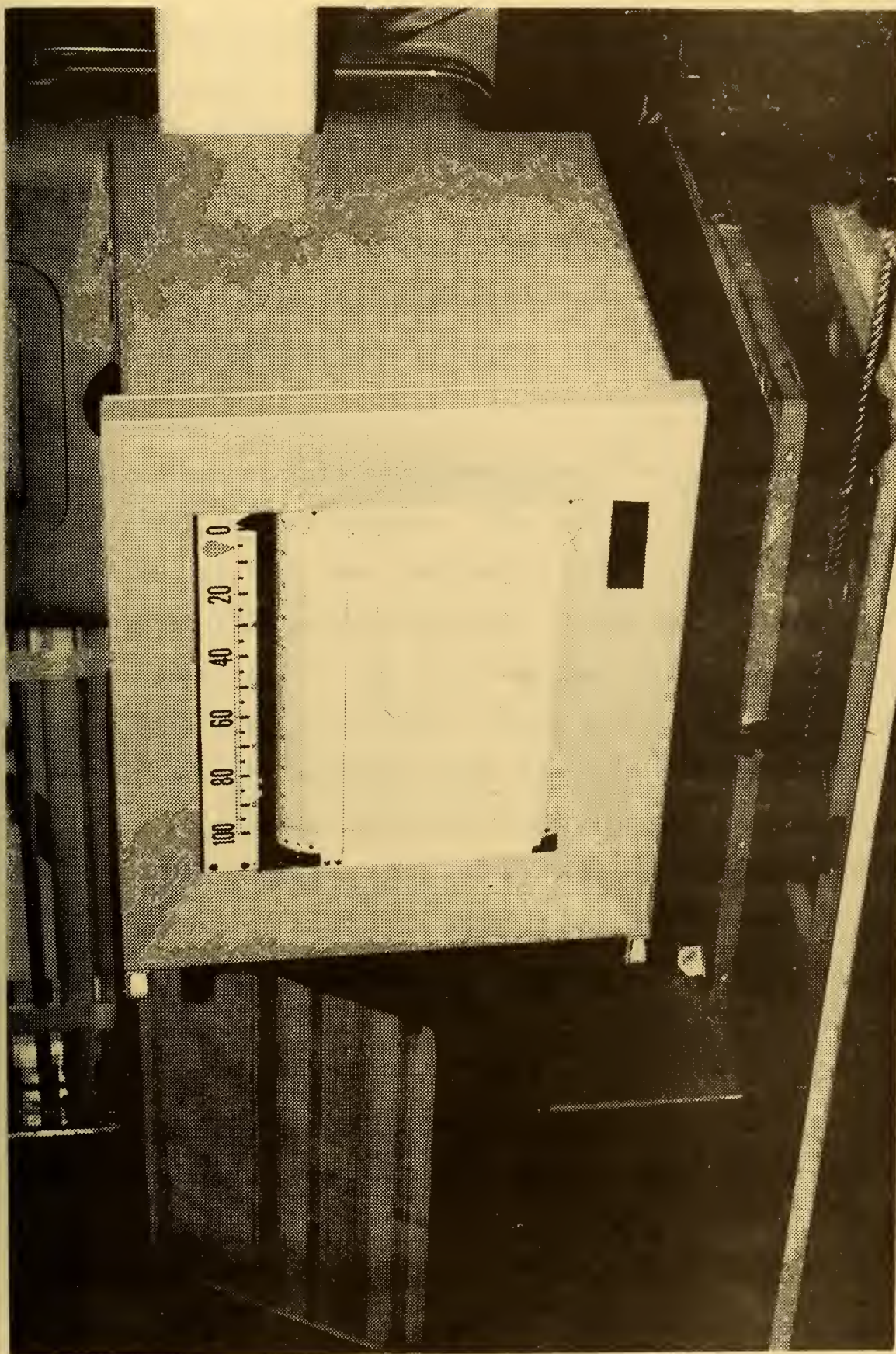


Figure 15. Shipboard Dual Pen Recorder Operation.

positioned so as to remain in place and not affect operation of the equipment.

The recorder was installed in case three. This component is quite heavy so rather than pad, as with the lighter components, the case was shock mounted on four heavy duty shock mounts. This prevented any damage from transportation or shipboard motion.

B. SAMPLING PROCEDURE

The nature of this study required a large number of surface or near surface samples. The simplest method of sample collection available was desired to simplify operation and minimize the time between samples. A 3/8 inch I.D. tygon tube was installed to the ship's engine room and attached to a salt water circulating pump casing vent. The selected pump was one with a short piping run from the sea suction located near the keel. This reduced chances of contamination from the piping system and was representative of the water immediately below the ship, least effected by ship motions and any ship discharge higher on the hull. The selected pump was required to be a continuously operating pump with a large flow rate which maximized water turnover and minimized any sampling time delays. The flow rate through the tubing was adjusted to about four liters/minute. The time delay for sample passage from the sea chest to the sampler was calculated as 13 seconds for this setup.

Samples were tested for contamination by comparing with Nansen bottle samples and deck pump samples taken from the depth of the engineroom sea chest. Results indicated all nutrient concentrations were the same within the precision of the technique and contamination was insignificant.

The sampling tube discharged a continuous flow into the sink. At the time desired, a sample cup was rinsed three times, filled from the tube and placed in the sampler. The time, depth and sample number was recorded on the data work sheet (Appendix A) for later correlation with the ships position.

Sampling through the mixed layer (to 100 meters) was performed using a deck operated gear pump with a garden hose attached to the hydro wire for varying depth of sampling. This pump also discharged into the sink and samples were taken in the same manner as above.

C. DIFFICULTIES AND PROBLEMS

During cruise four (see below) a submersible pump was obtained and used to collect samples through the mixed layer. This pump was lowered over the fantail to the desired depth and the water pumped to the surface. The results were satisfactory although the pump and hose weight became difficult to handle manually when 80-100 meters deep. Only three stations were obtained before the hose became entangled in the propulsion unit of the active rudder and the pump was lost. Subsequent depth samples were obtained using the deck pump as discussed above.

Some difficulties with bubble interference appeared to be related to ship roll during heavy seas. The sample stream must be debubbled prior to flowing through the cell or bubble spikes result on the recorder output. During heavy seas it seemed that the bubbles were not properly removed when the ship rolled. This problem was later identified as being caused by the use of an incorrect I.D. coupling used to join the reagent cartridge to the colorimeter. After the correct coupling was made up, ship roll did not affect the operation.

The time required to properly washout, exchange cartridges, change filters (and phototubes for the phosphate procedure), stabilize baseline and restandardize using fresh standards proved to be much longer than originally expected. An hour was normally required from completing one dual operation to commencing the next. This became a controlling factor when samples were being taken at short intervals (less than 10 minutes). When all required operations were included (washout, standardization, baseline checks, etc.), the time required to perform all four nutrient analyses on 80 samples was about 7 hours. This resulted in an average of 45 analyses per hour or about 11 samples per hour. If the sampling rate was greater than 11/hour for an extended time, samples began stacking up and were temporarily stored in the refrigerator.

All depth samples were taken while stopped. The suction hose was manually tied to the hydro wire as it was lowered

to 80 meters depth. When coming up the hose was handled by hand after being cut away from the wire. This procedure required two men and a considerable amount of time. During this period the ship drifted significantly in strong current areas, making accurate determinations of the vertical profile difficult.

D. FUTURE IMPROVEMENTS

To reduce the time required for cartridge changes and improve sampling techniques a number of improvements are under preliminary investigation:

1. An accurate study of standard deterioration is necessary to determine if DDDW standards show the deterioration reported for sea water and artificial standards. Preliminary results indicate no significant deterioration for over 24 hours if properly stored.

2. A combined standard may be possible [Strickland and Parsons 1968] which would further reduce the time required for shipboard operation.

3. A solenoid valve was obtained and an attempt to install in the flow line to automatically fill the sample cups looks promising and will reduce operator time. Difficulties with back pressure on the line now prevent operation.

4. A system of pumps set for different depths, each with a depressor attached, would allow depth samples to be taken when underway at a constant speed and allow greater selectivity of sample spacing and should produce results

less subject to ship drift from current effects. This method would also save much handling time and effort resulting in greater data output per operator.

V. CRUISE INFORMATION

During this study four cruises were performed to collect nutrient data. Table IV indicates the pertinent data associated with each cruise.

A. CRUISE ONE

Figure 16 illustrates the ship track followed for cruise one on 19 April 1972. The purpose for this cruise was to test the shipboard operation of the AA-II system and determine the variability of nutrient concentrations in the surface waters. Data were obtained for surface waters located eight feet below the surface (R/V ACANIA suction depth). The weather was extremely rough during this cruise and made depth sampling difficult. Four casts were performed to 40 meters and proved the feasibility of using a portable deck pump for sampling.

B. CRUISE TWO

Figure 17 illustrates the ship track followed for cruise two on 28 April 1972. During this season upwelling along the Monterey area coast was developing and cruise two was planned to obtain an early season upwelling signature. The weather was again rough with winds to 35 knots and sea/swell running 14-18 feet. This prevented all topside operations including vertical depth sampling. The performance of the internal sampling rig and AA-II system was satisfactory and good surface data were obtained.

TABLE IV

CRUISE DATA 1972

Cruise No.	Ship	From Time Date	To Time Date	No. Samples Collected	No. SiO ₄	No. PO ₃	No. NO ₃	No. NO ₂	Total Analysed
1	R/V ACANIA	1027 19APR	1624 19APR	33	33	0*	33	0*	66
2	R/V ACANIA	0800 28APR	1400 28APR	30	30	30	30	30	120
3	R/V ACANIA	1000 5 MAY	1615 5MAY	73	70	73	71	70	284
4	USNS BARTLETT	1425 18MAY	1500 21MAY	442	479	460	433	400**	1772

* Note: Equipment/Chemical problems prevented meaningful data.

**Note: Shortage of Ammonium Chloride Reagent prevented NO₂ Analysis during the last three hours of cruise four.

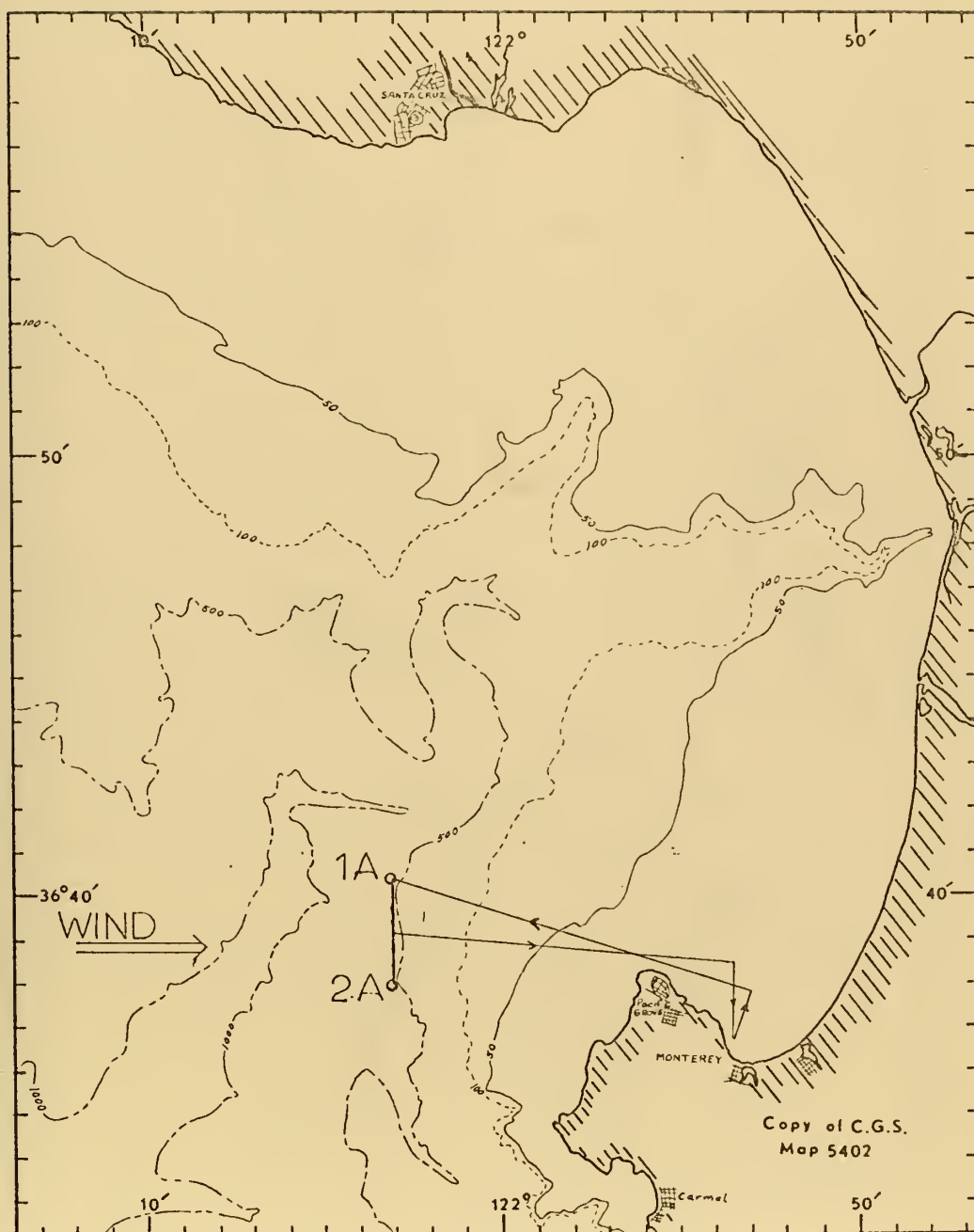


Figure 16. Exploratory Cruise Number One.
19 April 1972.

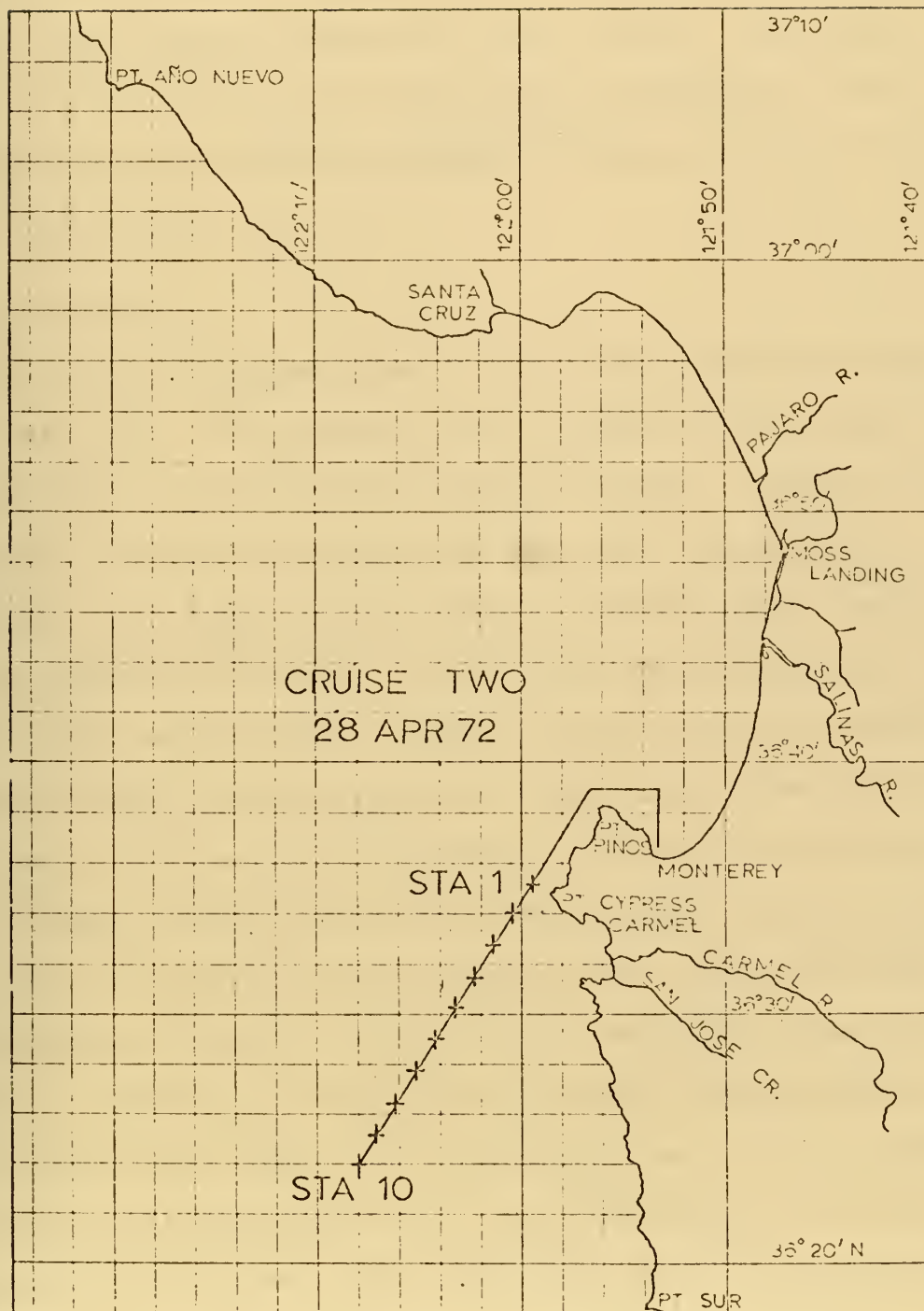


Figure 17. Cruise No. 2 Track 28 April 1972.

C. CRUISE THREE

Figure 18 illustrates the ship track for cruise three on 5 May 1972. This cruise gathered both surface and subsurface data inside the Monterey Bay circulation patterns. The weather was calm and the mixed layer stable. The data obtained were used to correlate the four nutrients with sampled areas and observe changes in nutrient concentrations with time of day.

D. CRUISE FOUR

Cruise four was performed on the USNS BARTLETT from 18 to 21 May 1972. This cruise was divided into six legs, the tracks were as illustrated in Figures 19-23. Track one was a general survey of the Monterey Bay area and used to correlate with data obtained during cruise three. Leg one was interrupted after the loss of the submersible pump (see Difficulties and Problems above) and the ship was forced to return to port for an underwater inspection. Leg two resumed on 19 May following the inspection. The purpose of this leg was to pass through and out of the shoreward upwelling area to a point 50 miles to sea to obtain open ocean nutrient concentration levels. The open sea levels were then to be used as a baseline to correlate with the higher concentration values near shore. In this manner upwelling strength and biological activity were to be determined by nutrient concentration changes. Data from legs three and four were obtained in this open sea area. Leg five returned shoreward

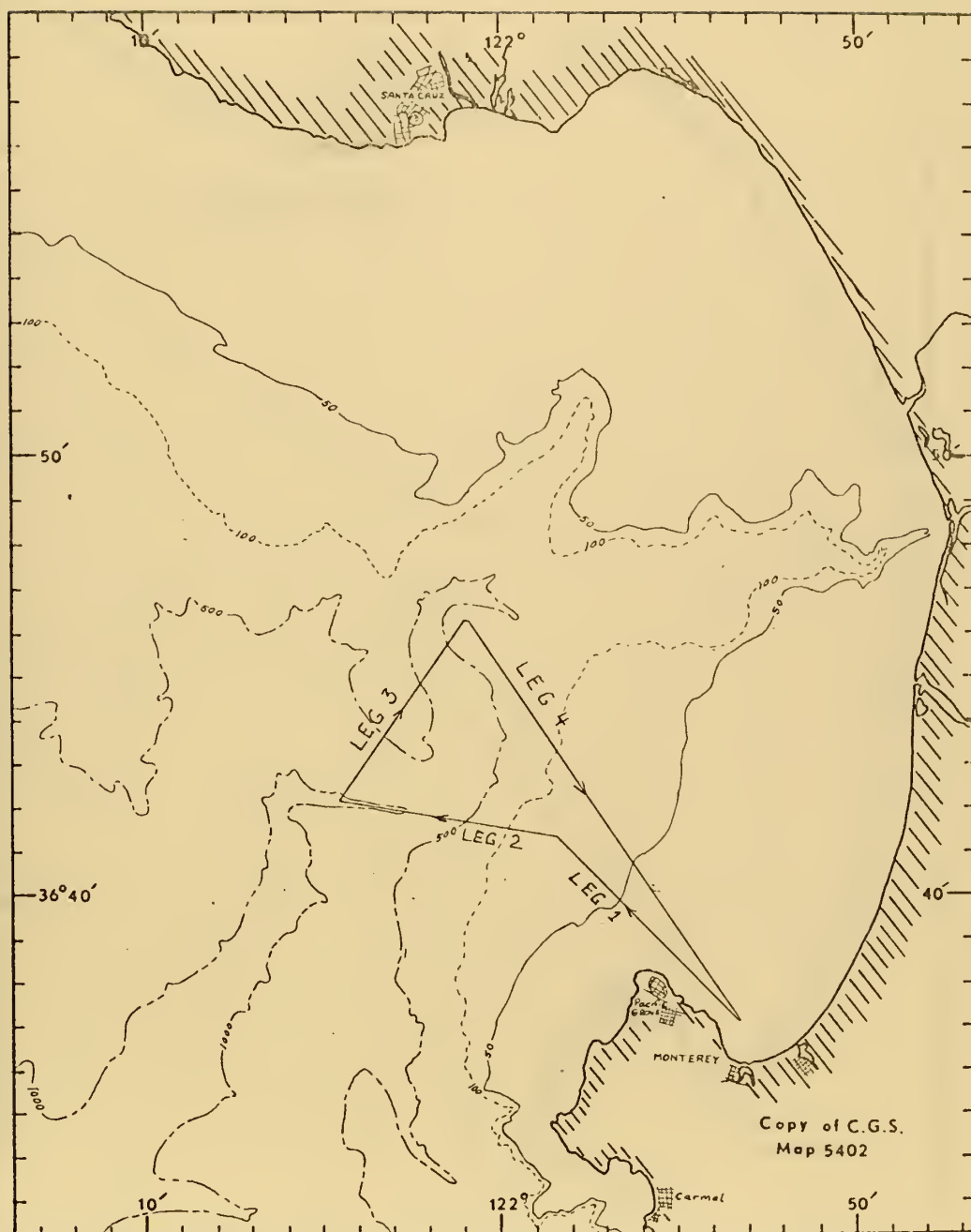


Figure 18. Cruise No. 3 Track 5 May 1972.

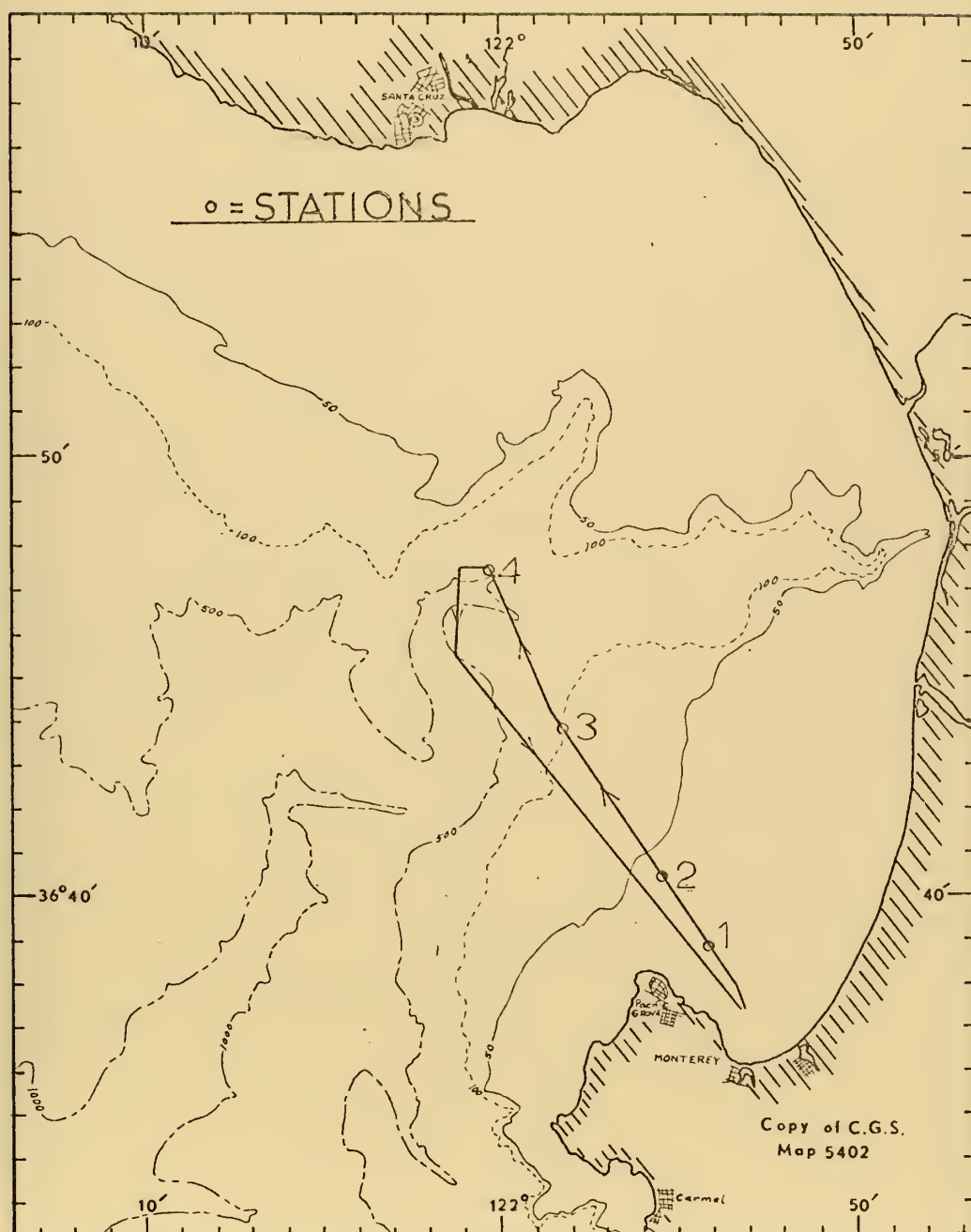


Figure 19. Cruise No. 4 Track Leg One 18-19 May 1972.

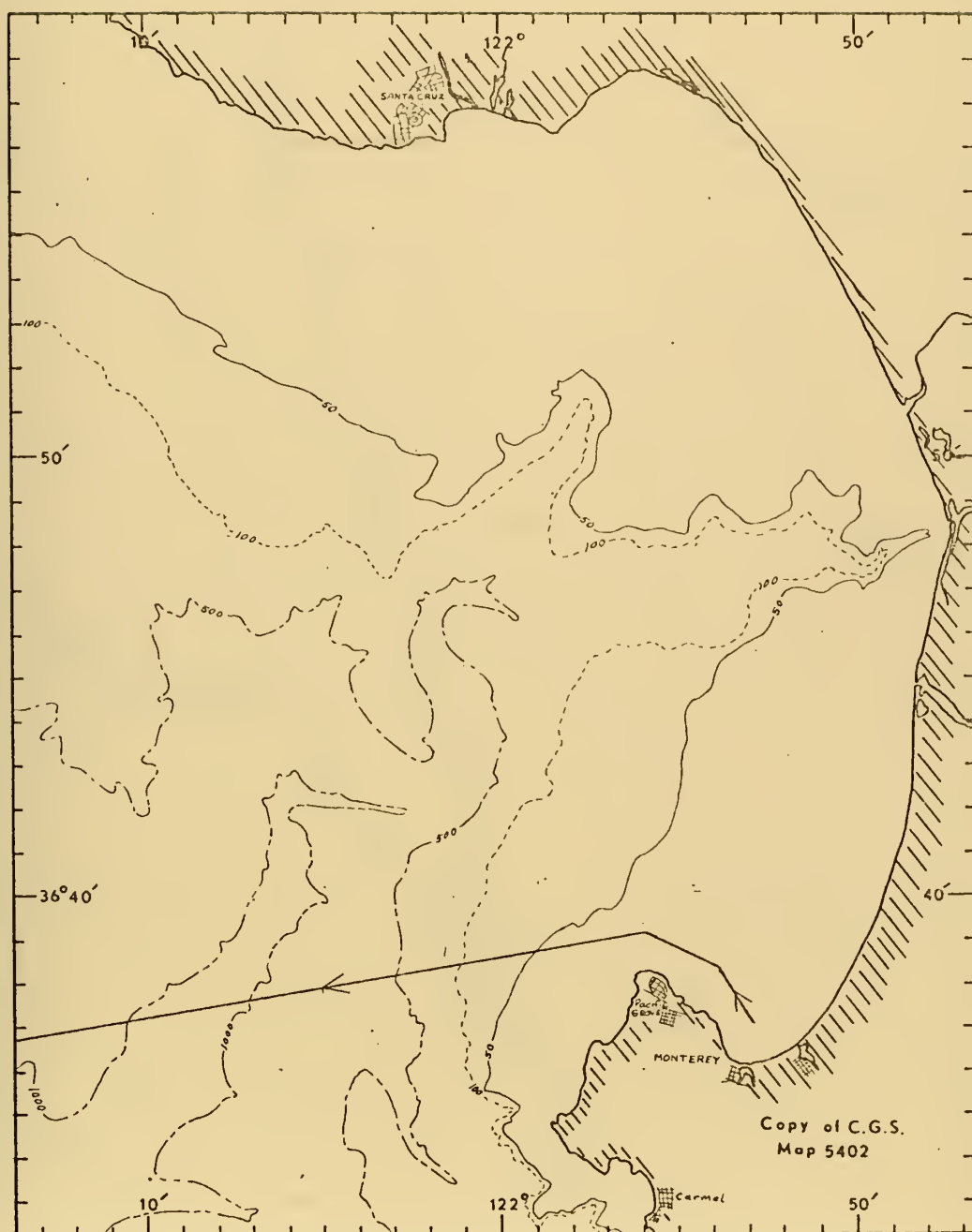


Figure 20. Cruise No. 4 Track Leg Two 19 May 1972.

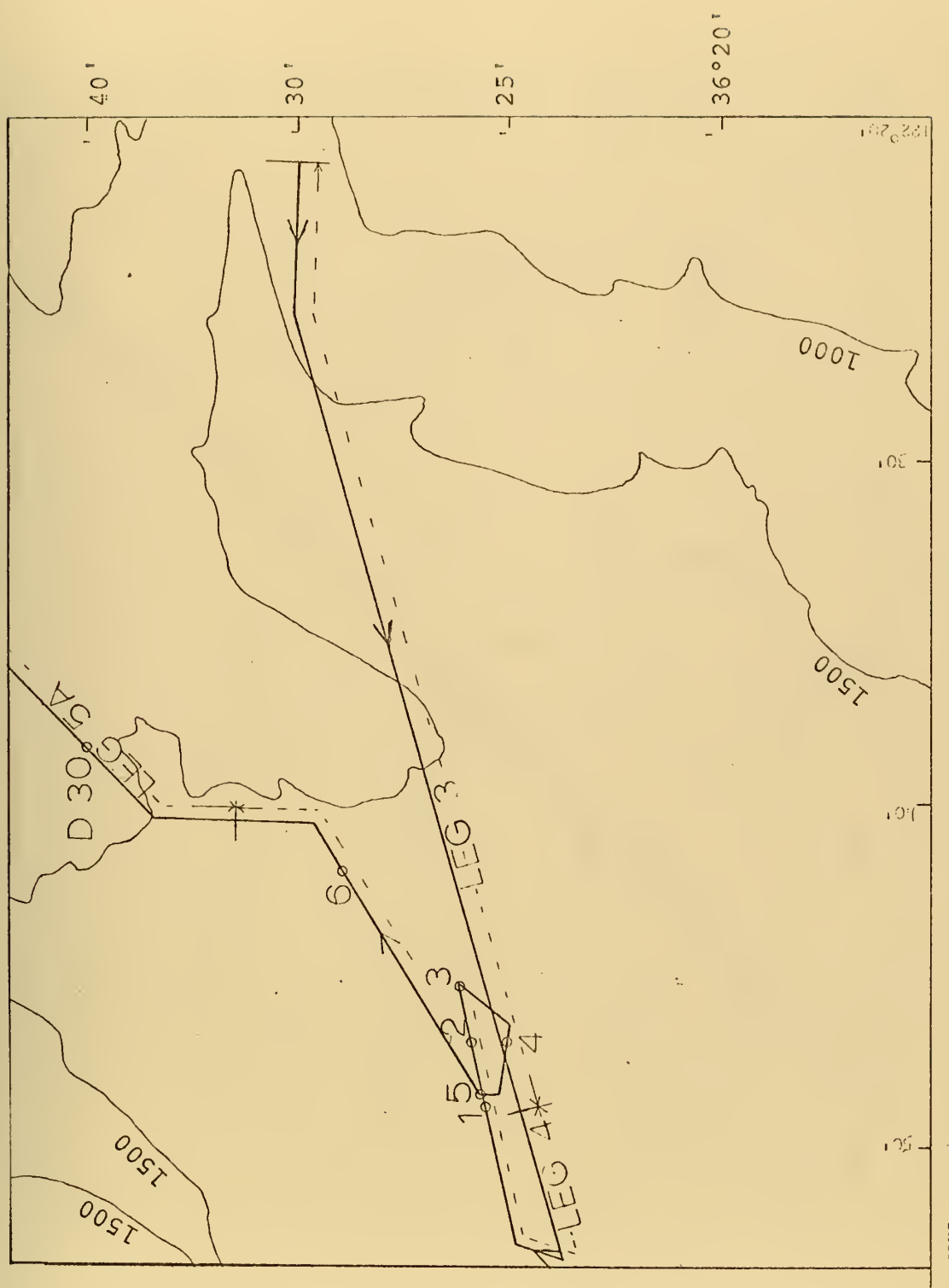


Figure 21. Cruise No. 4 Track Legs Three and Four 19-20 May 1972.

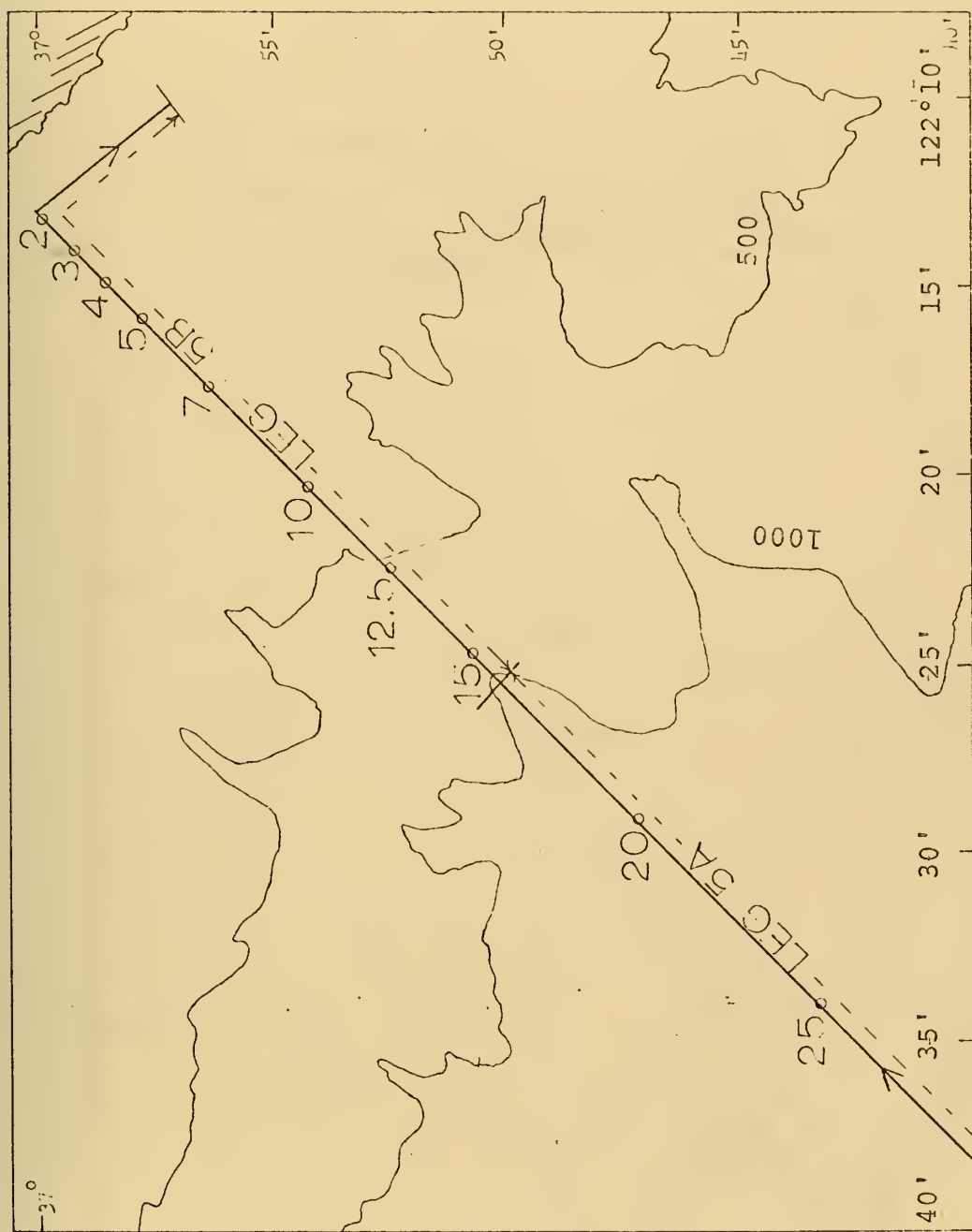


Figure 22. Cruise No. 4 Track Legs 5A and 5B 20-21 May 1972.

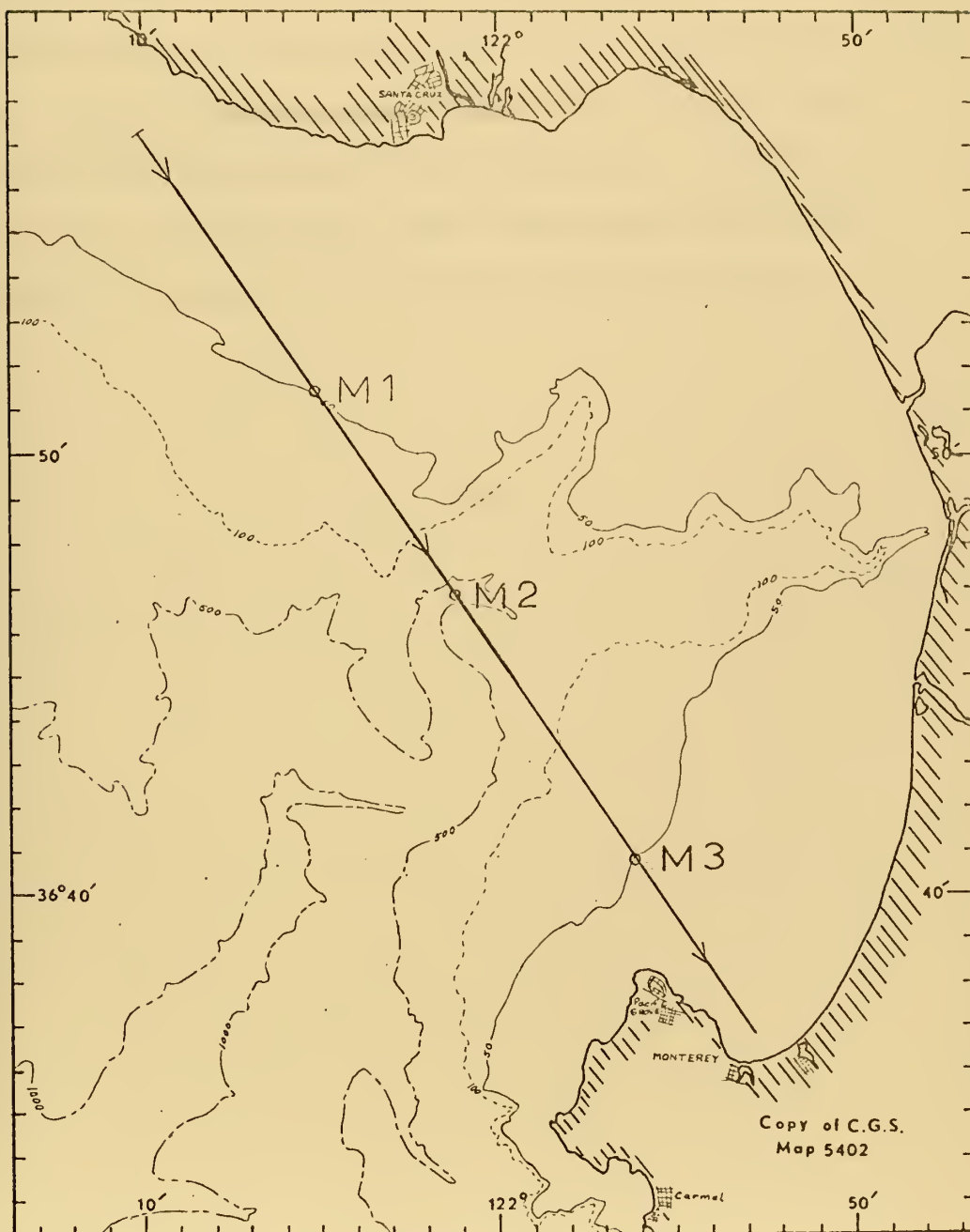


Figure 23. Cruise No. 4 Track Leg Six 21 May 1972.

obtaining a nutrient signature of a different upwelling area. Finally, leg six passed across Monterey Bay again furnishing bay area variation data.

Operations during the cruise four period furnished the bulk of the data for this study. All surface samples from the installed tube system were taken at a depth of 13.5 feet of water. Vertical temperature data were obtained with Expendable Bathythermograph (XBT) equipment. Particle density, light transmittance, and chlorophyll data were obtained and are presented elsewhere [Killion 1972].

VI. RESULTS

A. SURFACE DATA

1. Cruise One

Cruise one results were rather disappointing due to bad weather, equipment difficulties, and chemical problems. Satisfactory results of only the silicate and total nitrate analyses were obtained and are presented in Figure 24. Phosphate values were not obtained due to chemical problems with the color reagent which prevented satisfactory calibration and caused an unstable baseline. This problem was believed caused by a bad ascorbic acid reagent. This reagent was prepared fresh for each subsequent cruise. Figure 24 indicates the silicate and total nitrate variation in the surface waters of the two mile track between points 1A and 2A of Figure 16. The distance is plotted from the initial point 1A. This track was selected perpendicular to the wind direction outside the area of expected upwelling. Both the silicate variation ($0.8 \mu\text{gat Si/l}$) and the total nitrate changes ($0.20 \mu\text{gat N/l}$) were found to be very small and could be considered near constant within the accuracy of the analysis techniques. These results indicate a very well mixed water mass which was confirmed by isothermal BT traces and a weather history of heavy seas for the previous five days.

+ = Inorganic Silicate
 o = Total Nitrate

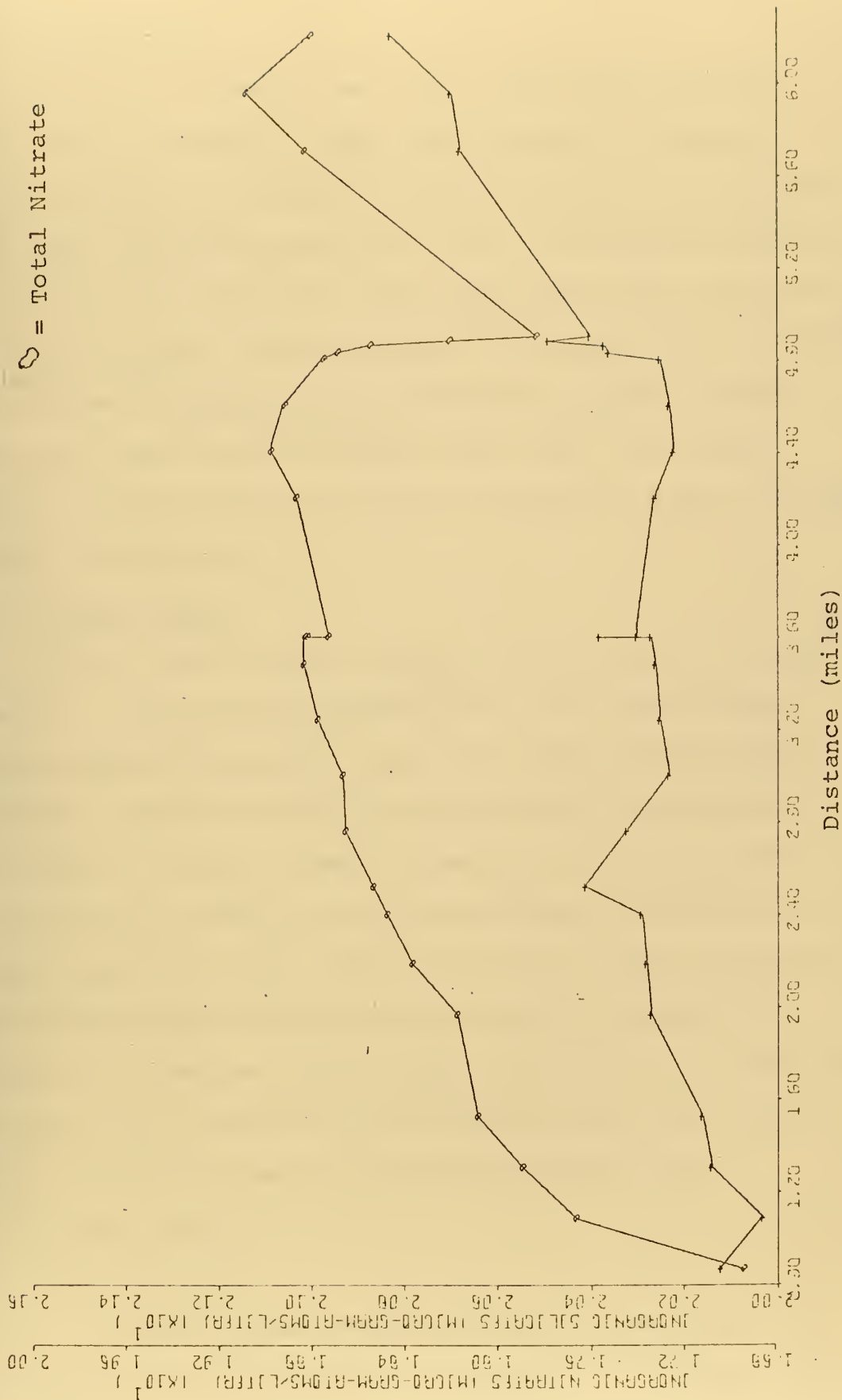


Figure 24. Nutrient Concentrations Versus Distance - Cruise #1.

2. Cruise Two

Cruise two results were very interesting and are illustrated in Figure 25. Here the distance is measured along the track from station 10 toward Monterey Bay (Figure 17). Station separation was one mile. An upwelling signature was obtained where all three major nutrient concentrations (SiO_4 , PO_4 , NO_3) first increased shoreward, then remained quite constant, finally rapidly decreasing across the 100 fathom curve and into the Monterey Bay area. The major nutrient concentrations indicated an extremely close, although expected, correlation.

3. Cruise Three

Cruise three surface data is illustrated in Figures 26 and 27. A significant variability in the three major nutrient concentrations was found over most of the track. A five mile length of track (distance eight to ten miles along track), however, showed a constant nutrient plateau. This plateau was found in the area analysed in cruise one although sampled 16 days later. The three major nutrients tested varied almost identically as noted in cruise two. The results of leg one show a close relationship to the last half of leg four (distance 22 to 27 miles) where the tracks nearly coincided but were analysed five hours apart.

4. Cruise Four

a. Leg One

Surface data obtained during cruise four, leg one (Figure 19) is illustrated in Figure 28. A significant

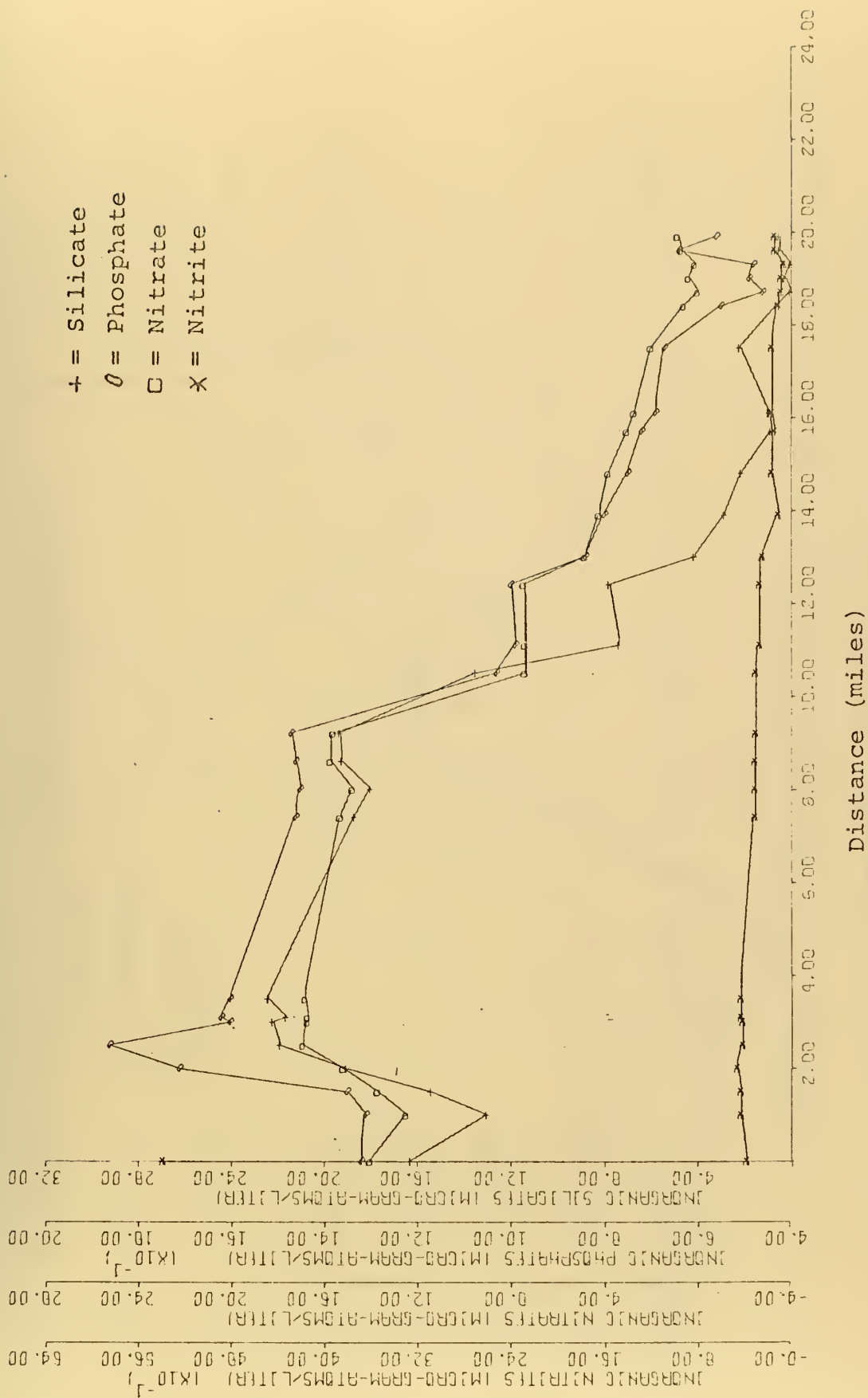


Figure 25. Nutrient Concentrations Versus Distance - Cruise #2.

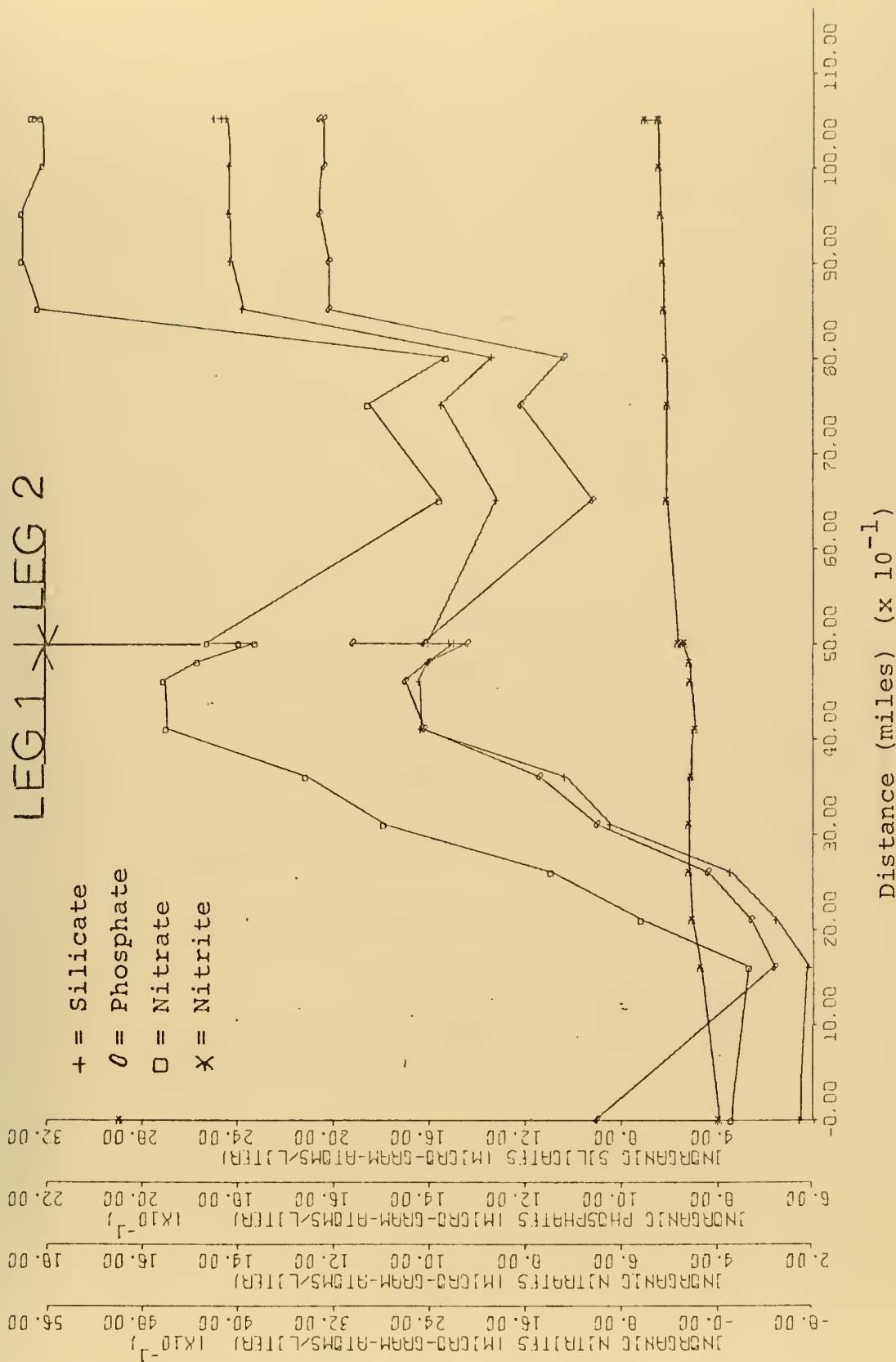


Figure 26. Nutrient Concentrations Versus Distance - Cruise #3 Legs One and Two.

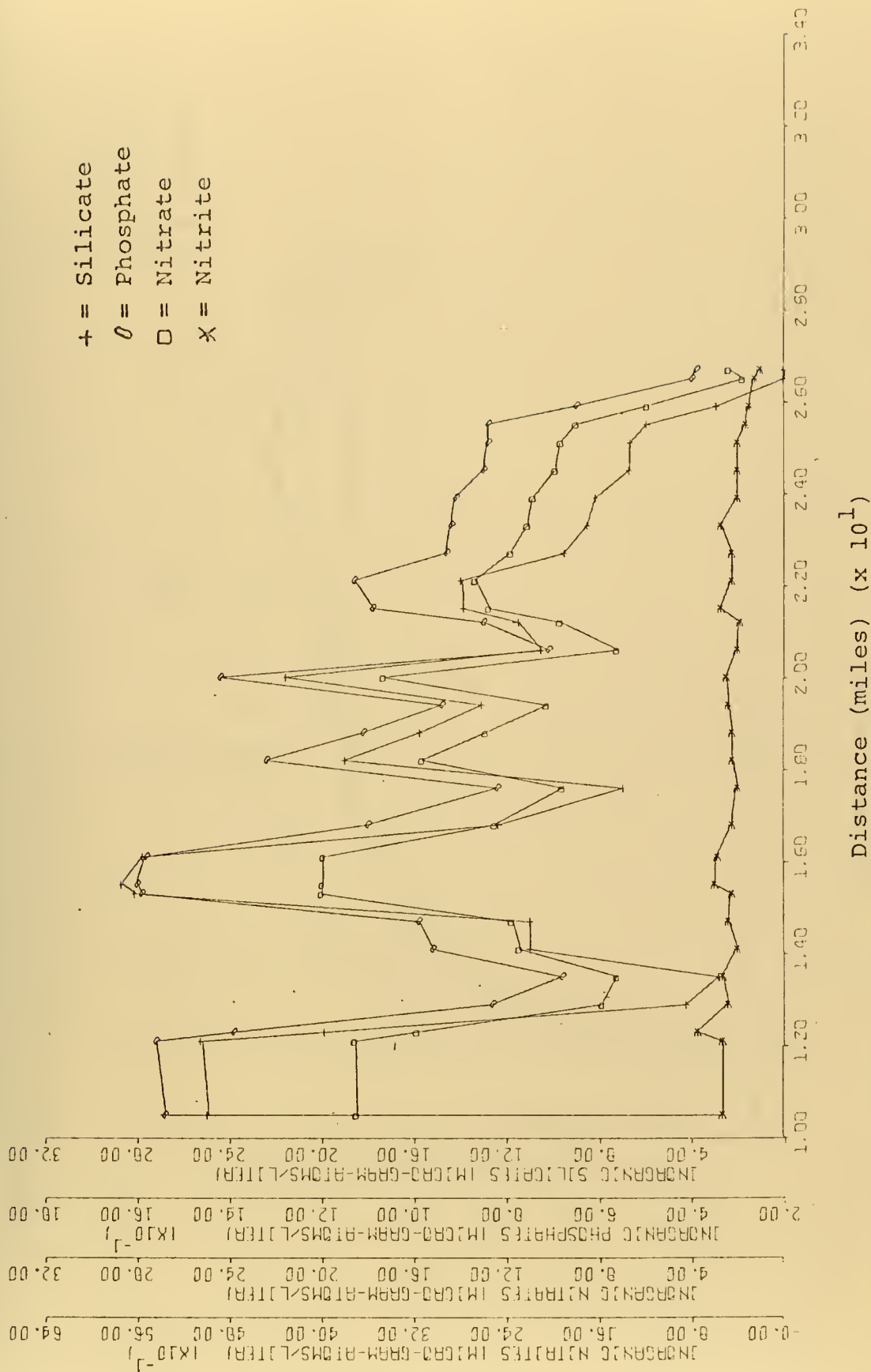


Figure 27. Nutrient Concentrations Versus Distance - Cruise #3 Legs Three and Four.

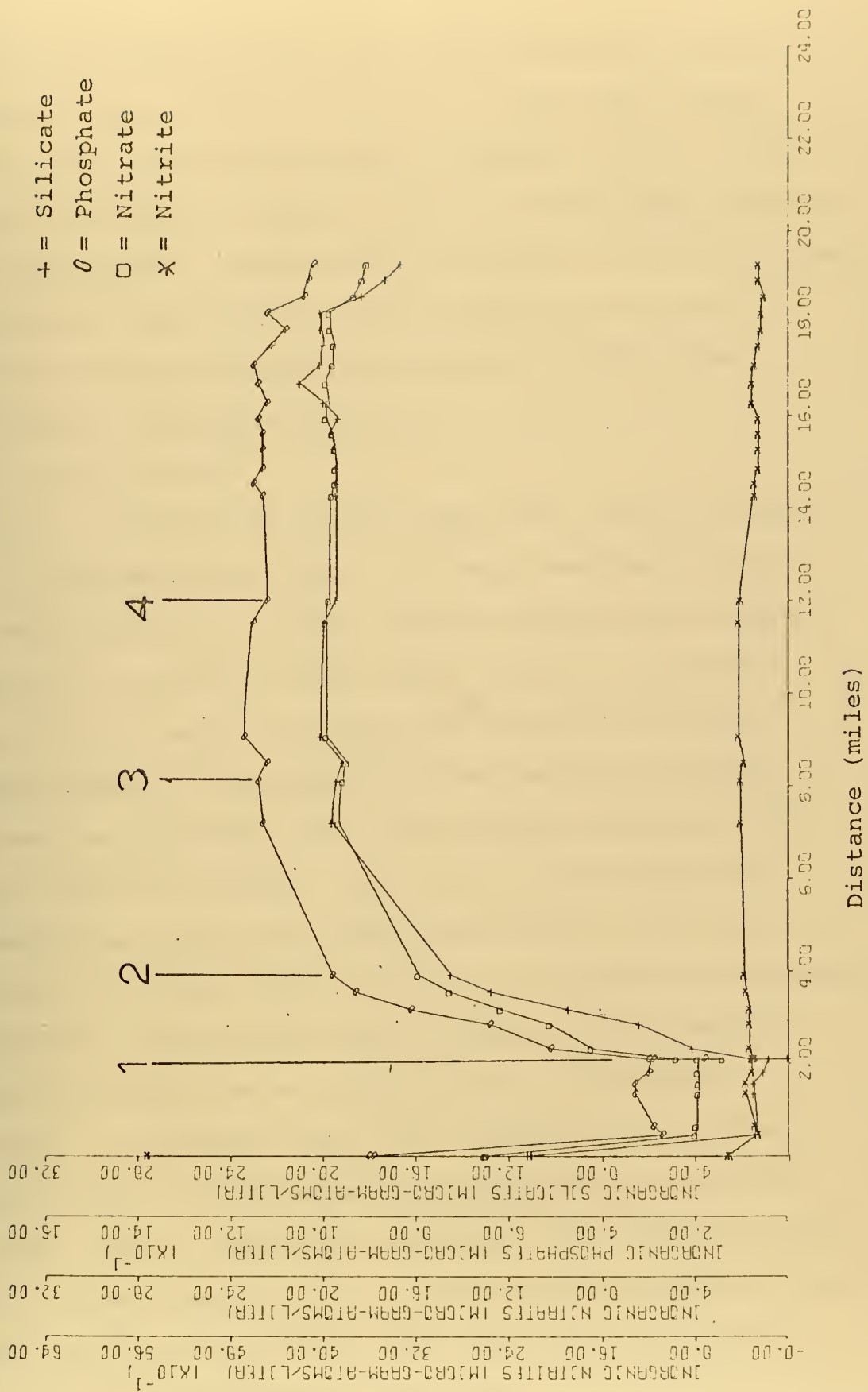


Figure 28. Nutrient Concentrations Versus Distance - Cruise #4 Leg One.

change in the Bay nutrient signature was found from that obtained 12 days earlier (cruise 3). The level plateau noted previously had developed in Monterey Bay and existed across the submarine canyon to the 50 fathom curve (station 2). The nutrient signature for the harbor to 50 fathoms had not changed significantly. This plateau pattern again identifies the well mixed high nutrient surface layer indicative of developed upwelling.

b. Leg Two

Surface data from cruise four, leg two (Figure 20) is illustrated in Figure 29. When compared to cruise two data (Figure 25), these results indicate the changing upwelling signature 21 days apart. The major nutrients (SiO_4 , PO_4 , NO_3) were still very well correlated but the plateau values for phosphate had decreased 23% and for silicate had decreased 27%. The average nitrate plateau values remained constant. The width of the upwelling signature had grown from about seven miles (cruise two) to 13 miles for cruise four, leg two. An interesting phosphate maximum was found on the seaward edge of both upwelling areas and appears to correspond with high biological activity. Chlorophyll data from cruise four indicated a rapid increase in chlorophyll concentration at 18 miles [Killion 1972]. This high chlorophyll level was maintained for 28 miles along the track. Indications of plankton bloom areas were found to clearly correlate with the minimum nutrient concentrations in this area.

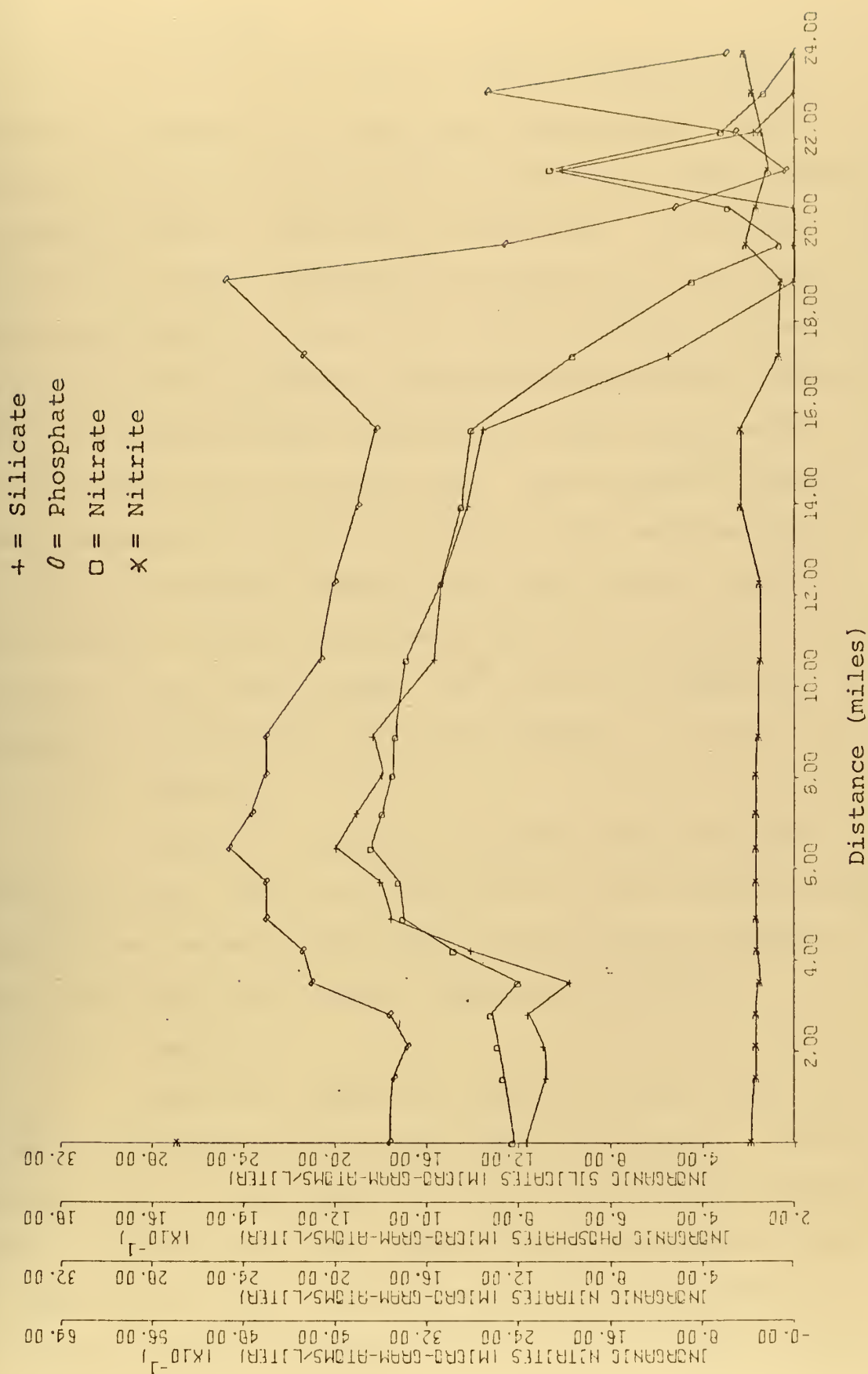


Figure 29. Nutrient Concentrations Versus Distance - Cruise #4 Leg Two.

c. Leg Three

Surface data from leg three (Figure 21) is presented in Figure 30. A four mile continuation of the nutrient low found on leg two is followed by a rapid increase to another nutrient high over 14 miles wide. Inside this area of high surface nutrient concentration the chlorophyll values were found to be very low. Major nutrient concentrations continued to provide outstanding correlations. Plateau values had changed significantly from values found on the leg two plateau only 12 miles away. The phosphate concentration decreased 33% whereas silicate (47% decrease) and nitrate (44% decrease) changes were nearly equal. At 45 miles another plankton bloom was found driving surface nutrients to near zero values. This two mile bloom was followed by another three mile wide plateau.

d. Leg Four

Figure 31 illustrates surface data obtained from cruise four, leg four (Figure 21). Again three plateaus were obtained between which were strong planktonic blooms which had driven the nutrient concentrations down.

e. Leg Five

Leg five (Figure 22) was divided into two sections 5A (72 to 90 miles) and 5B (90 to 110 miles). Leg 5A surface data is illustrated in Figure 32 and clearly indicates a continuation of the bloom-plateau signatures found in legs four and five. Leg 5B surface data is illustrated in Figure 33 and is representative of another well developed

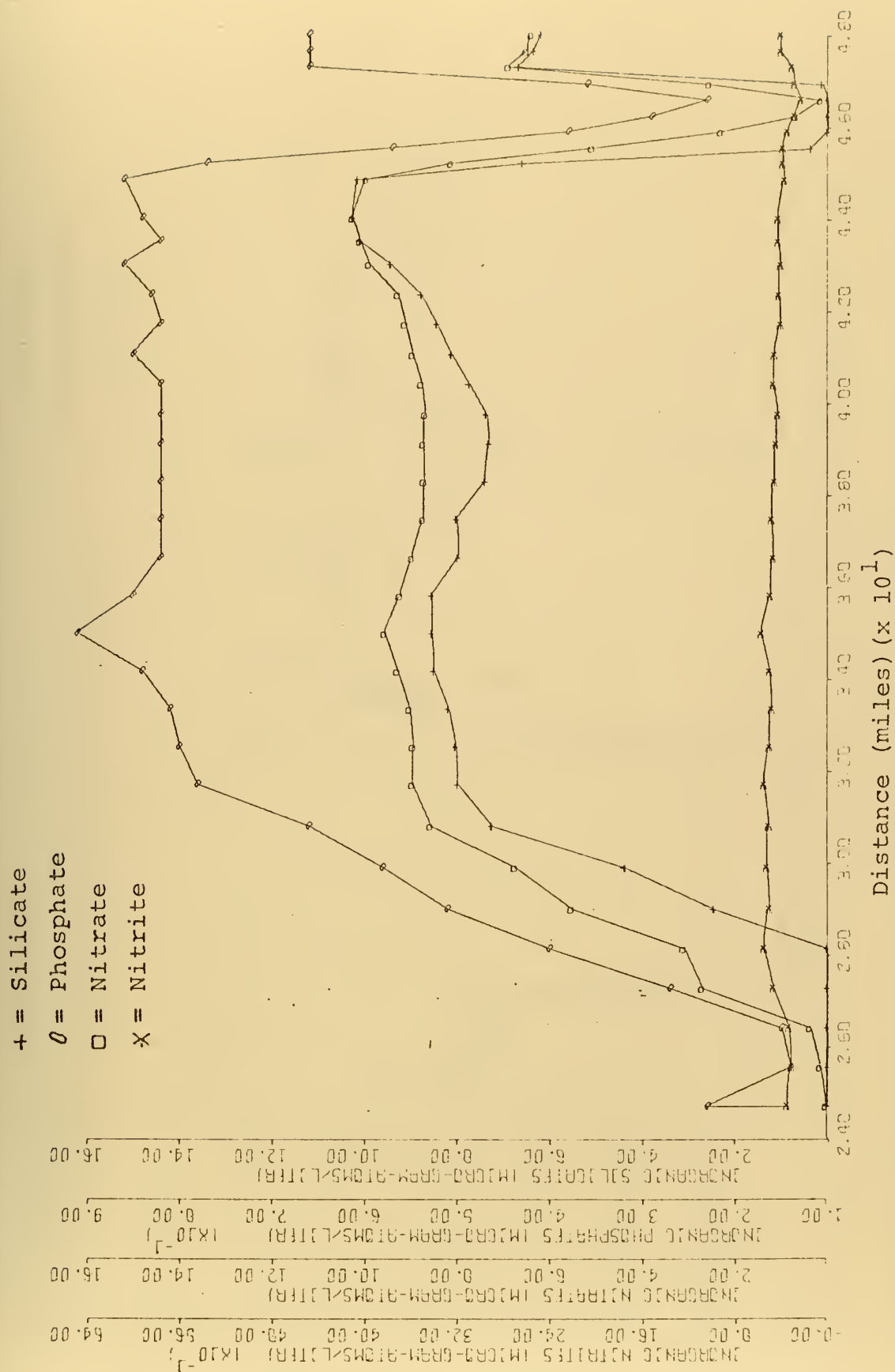


Figure 30. Nutrient Concentrations Versus Distance - Cruise #4 Leg Three.

+ = Silicate
 0 = Phosphate
 □ = Nitrate
 x = Nitrite

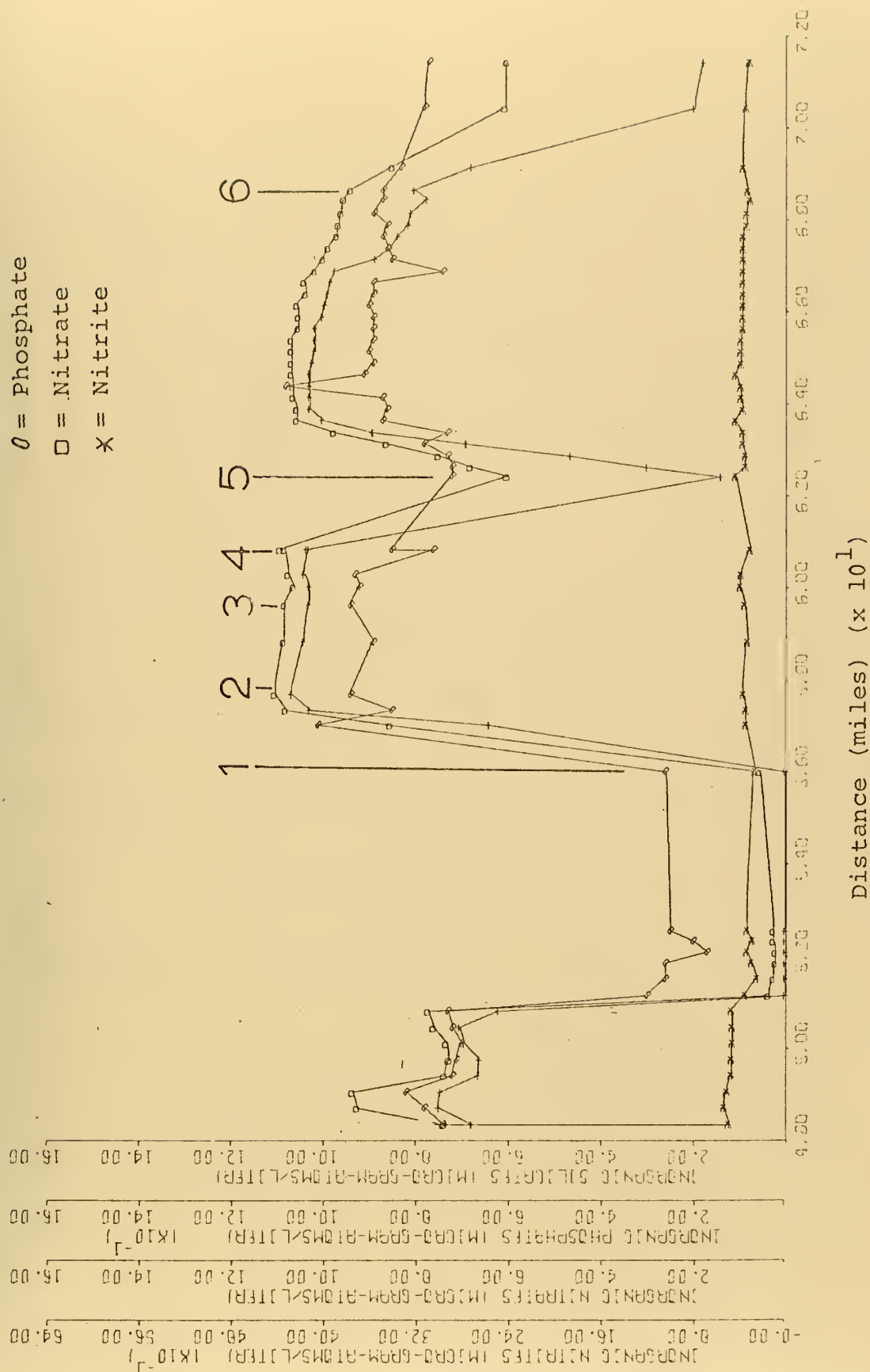


Figure 31. Nutrient Concentrations Versus Distance - Cruise #4 Leg Four.

+ = Silicate
 O = Phosphate
 □ = Nitrate
 X = Nitrite

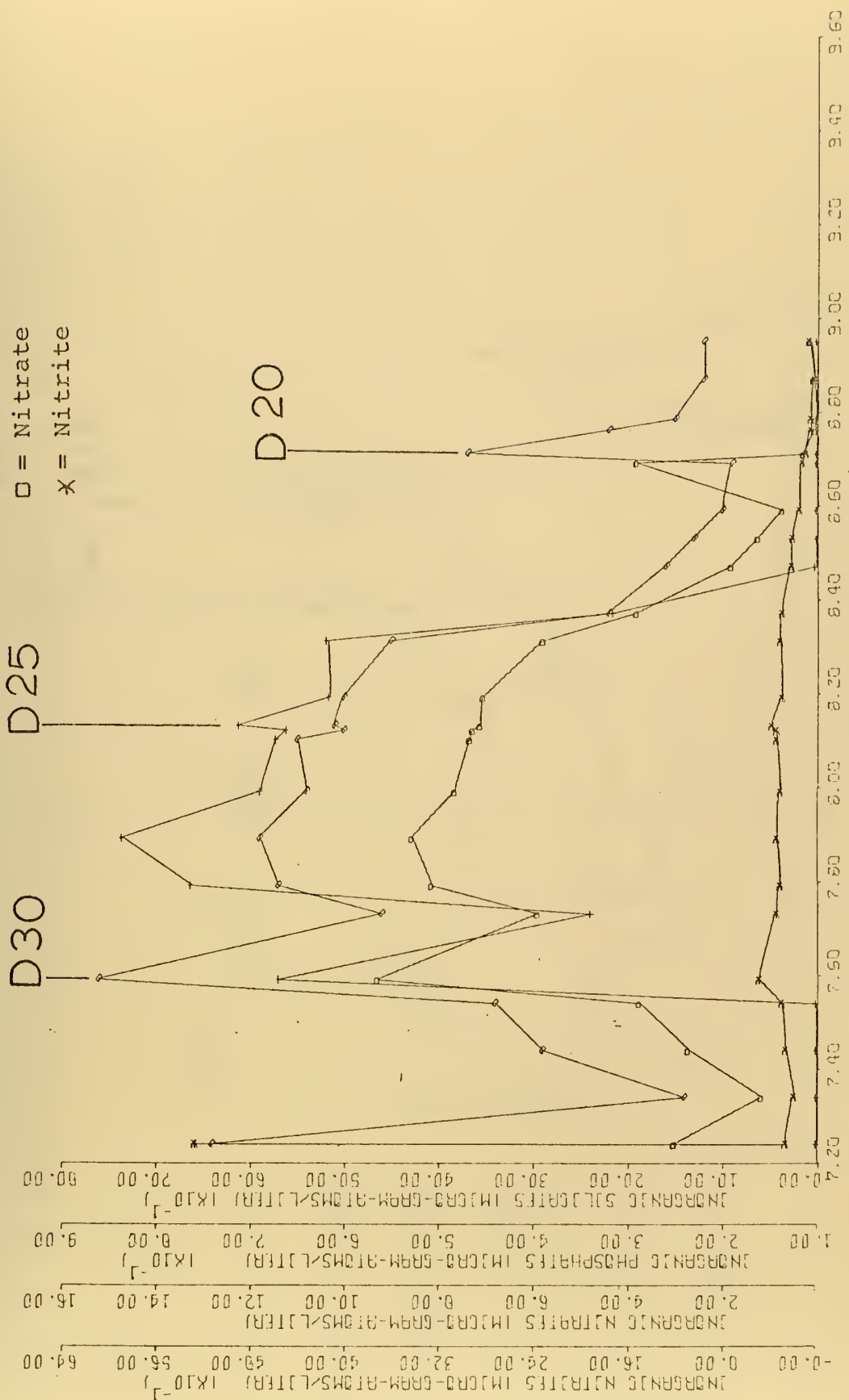


Figure 32. Nutrient Concentrations Versus Distance - Cruise #4 Leg 5A.

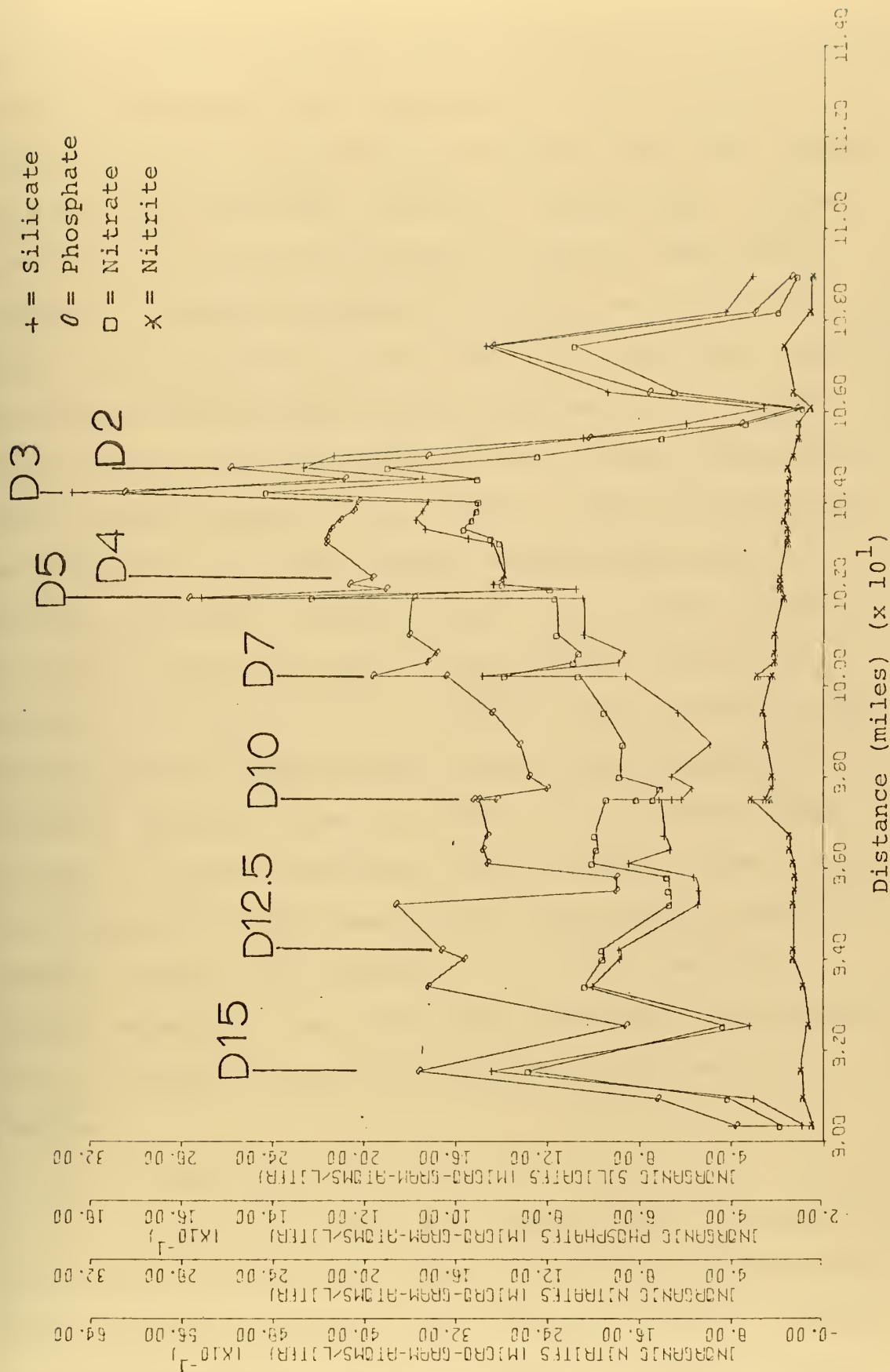


Figure 33. Nutrient Concentrations Versus Distance - Cruise #4 Leg 5B

upwelling signature 14 miles wide increasing in concentration levels as the coastline is approached. After completion of station D-2 (two miles from the coastline) the track turned and paralleled the coast. Nutrient concentrations dropped significantly in this area (from 105 miles along track) indicating a reduced upwelling intensity due to shallow water. Station positions D-30, D-15, D-7, D-5, D-3, and D-2 show peak surface values for the major nutrients significantly greater than surrounding waters. These spikes were first believed caused by the differing sampling techniques. The installed tube system showed reduced values and the portable deck pump indicated higher concentrations during the vertical determinations. The vertical profiles (see Vertical Variations) later proved that the different equipment was not at fault but the actual concentrations dramatically decreased from the surface to 13.5 feet. This decrease in values correlated with the spike values noted. This unexpected result does distort the surface signature somewhat because all surface and 13.5 foot samples are plotted together. The results are significant and real and will be further discussed when presenting the vertical profiles.

f. Leg Six

Leg six (Figure 23) surface data is illustrated in Figure 34. This final leg of cruise four represents the profile across the Monterey Bay submarine canyon. A rapid increase in concentrations was noted at 109 miles as the

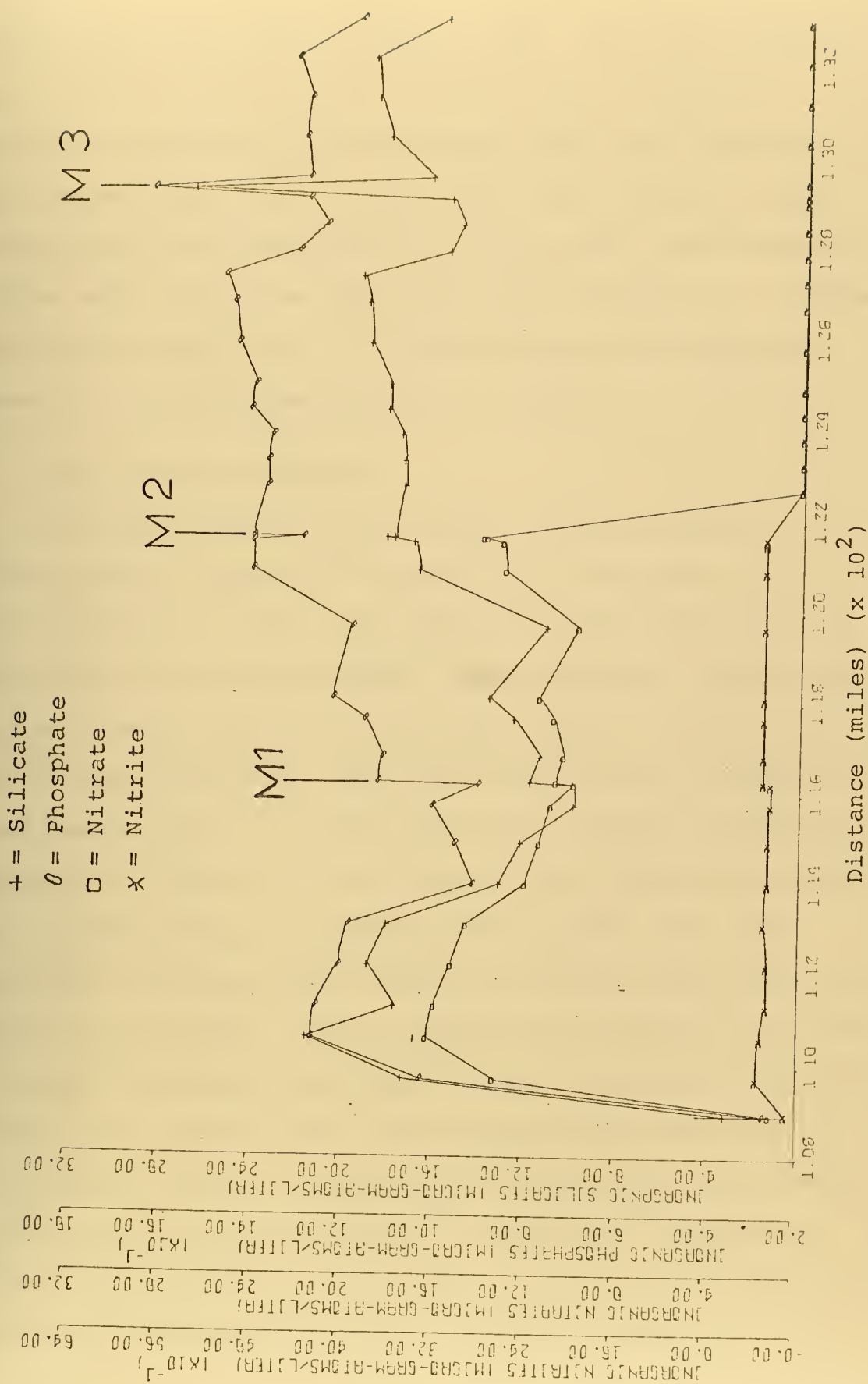


Figure 34. Nutrient Concentrations Versus Distance - Cruise #4 Leg 6.

track moved away from the coastal area. This was followed by a slower increase to the plateau values reached at station M2 directly over the deepest water (500 fathoms). The southern half (122 to 132 miles) again shows the constant plateau area described in leg one with concentration values much like those found three days previously. Nitrate and nitrite data from 122 to 132 miles was not obtained because of insufficient reagents on board.

B. MIXED LAYER VARIATIONS

Cruise four mixed layer nutrient concentrations are illustrated in Figures 35 through 41. Each figure is a horizontal plot of the three major nutrient (SiO_4 , PO_4 , NO_3) concentrations versus distance along the track. Each figure presents data at one of seven depth sampled; 10, 20, 30, 40, 50, 60, and 70 meters. The first 50 miles was not significant because of lack of data but does indicate the general variation. From 50 to 130 miles the data were more complete and the mixed layer variations were clearly seen. The nutrient variations were found to be quite similar for all depths to 50 meters. Close examination of the 50, 60, and 70 meter variations indicated a lesser correlation with the near surface results and a more significant effect from circulation patterns, especially the upwelling area from 85 to 105 miles along the track. The depth of the seasonal thermocline was found to be from 25 to 45 meters near land and near 50 meters at stations farther to sea.

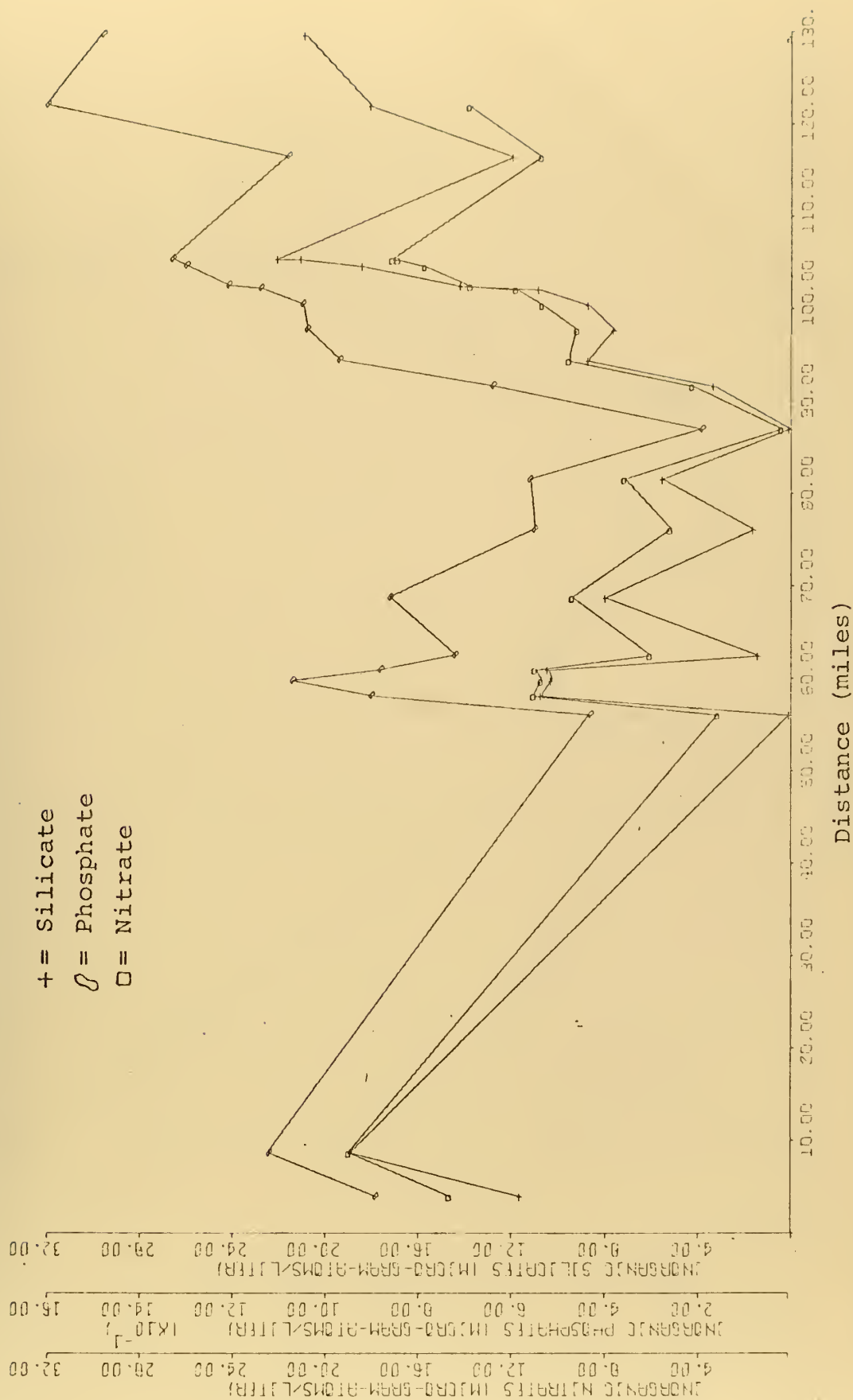


Figure 35. Nutrient Concentrations Versus Distance-- Cruise #4 10 Meters Depth.

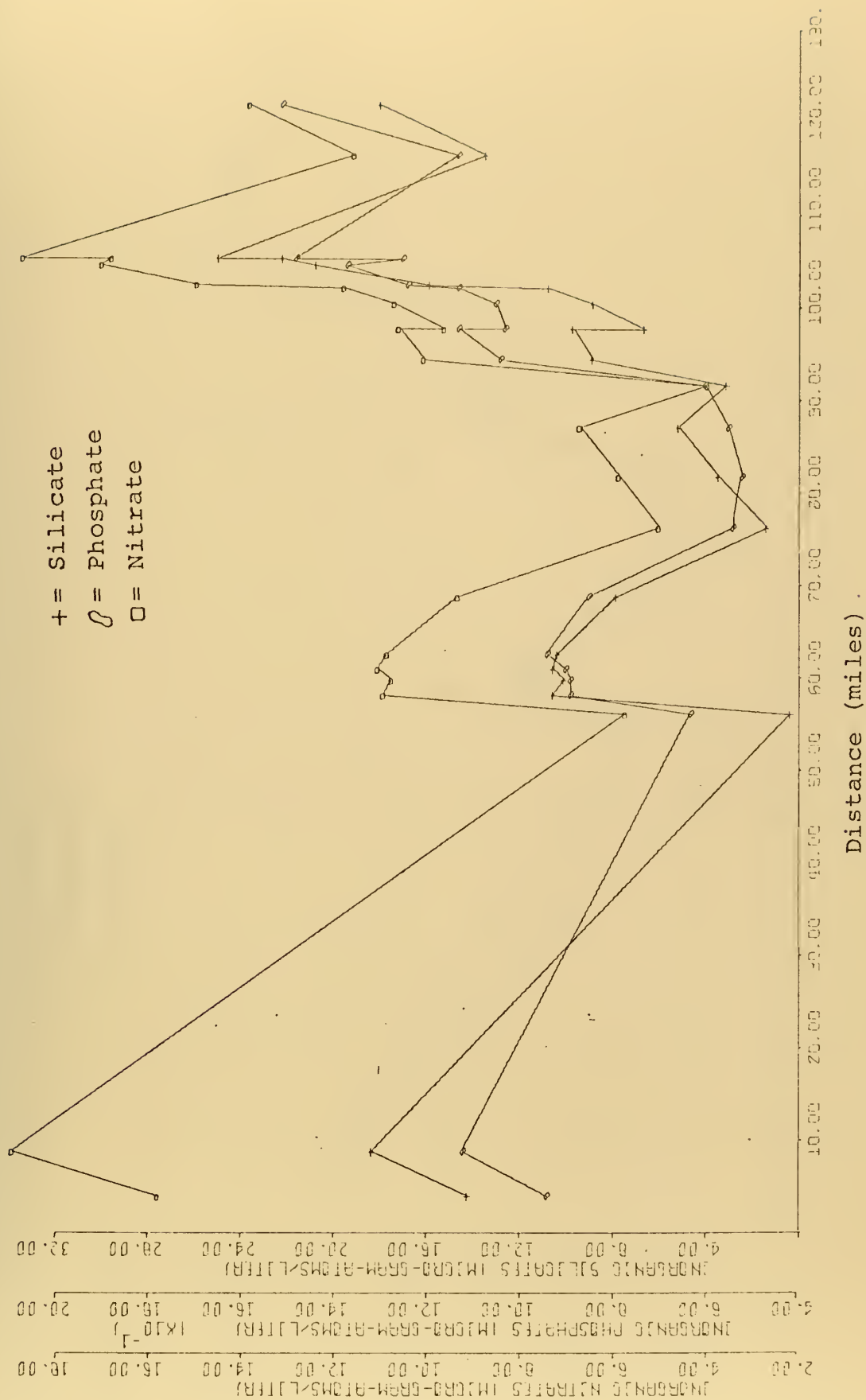


Figure 36. Nutrient Concentrations Versus Distance - Cruise #4 20 Meters Depth.

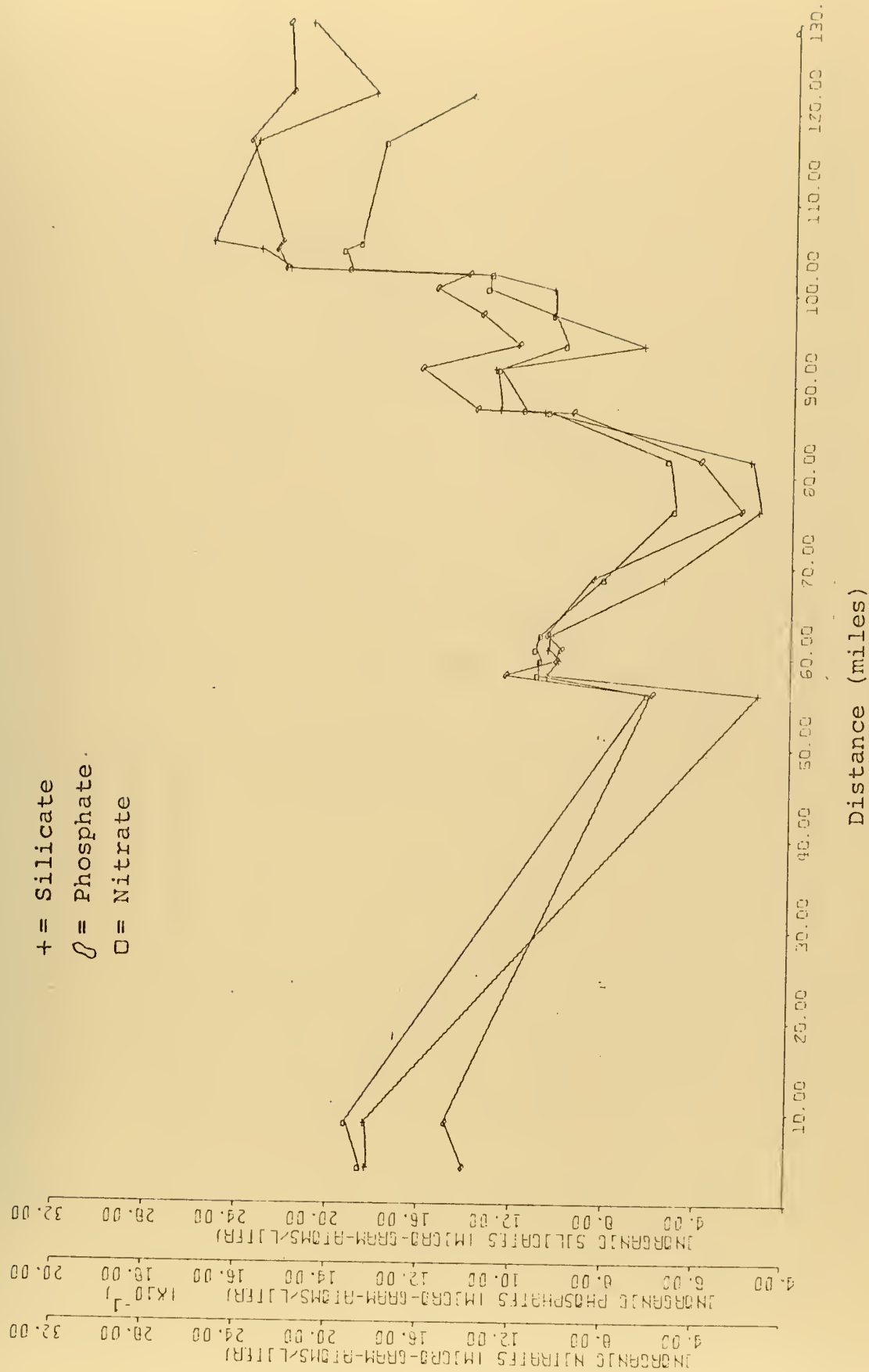
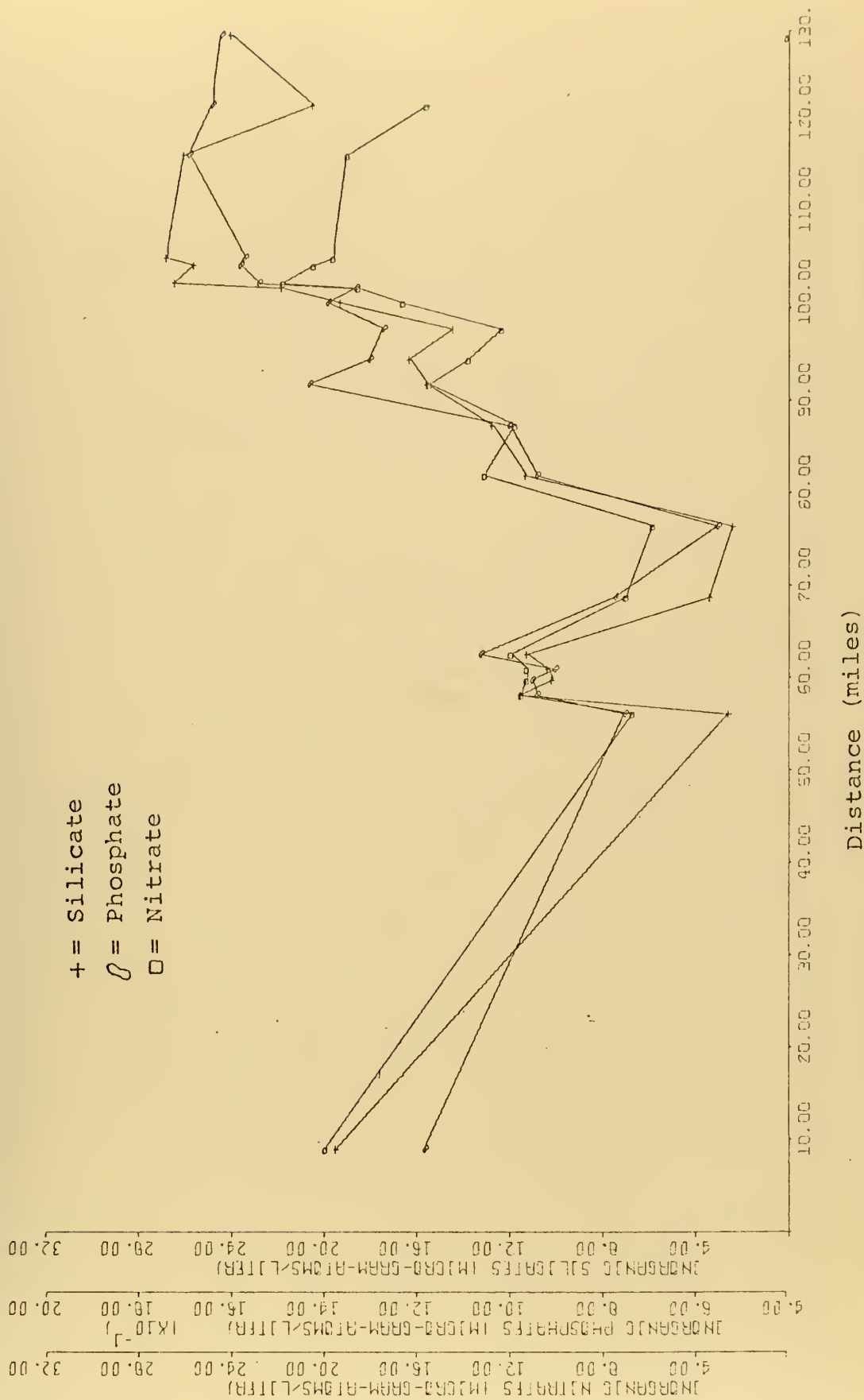


Figure 37. Nutrient Concentrations Versus Distance - Cruise #4 30 Meters Depth.



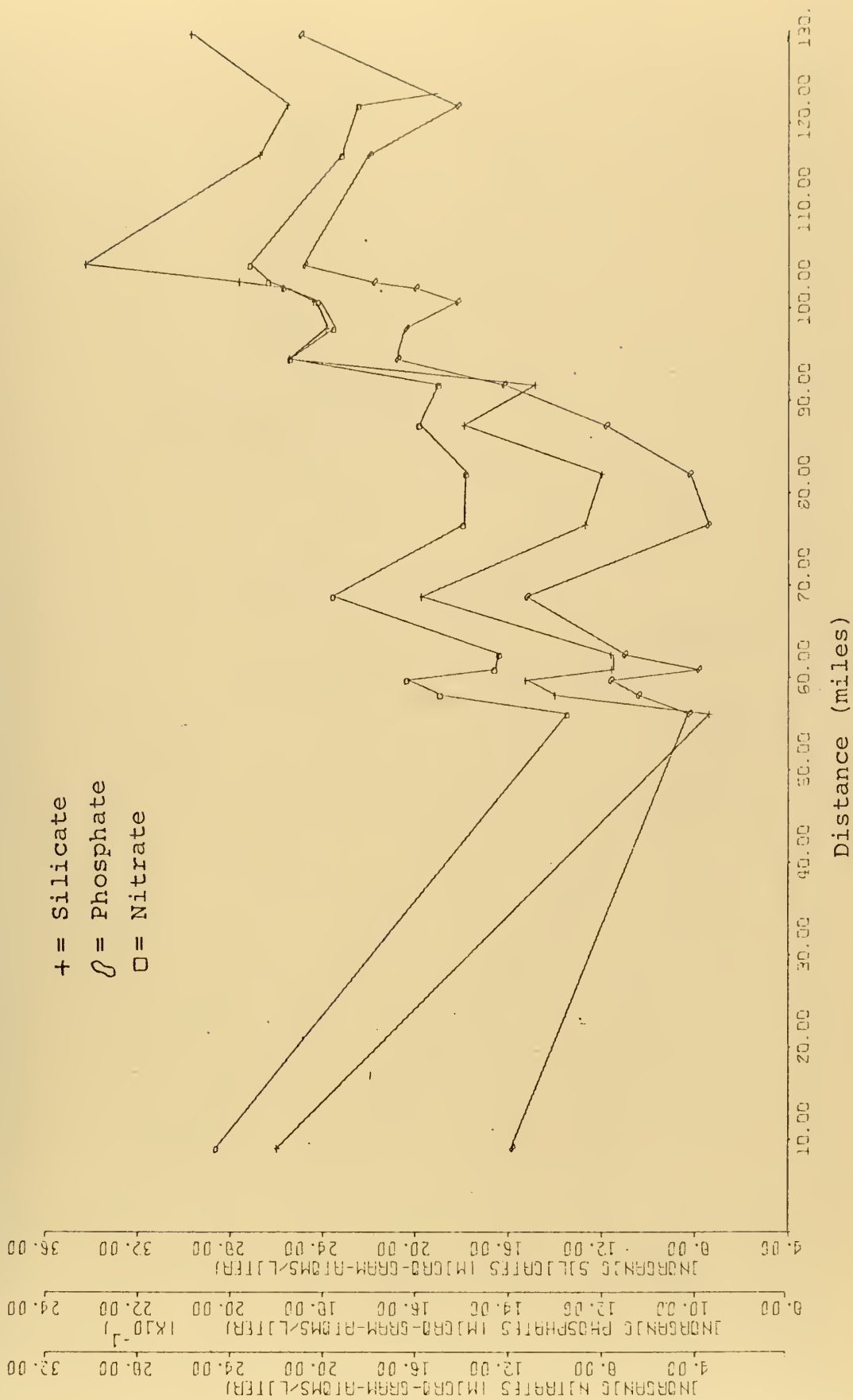


Figure 39. Nutrient Concentrations Versus Distance - Cruise #4 50 Meters Depth.

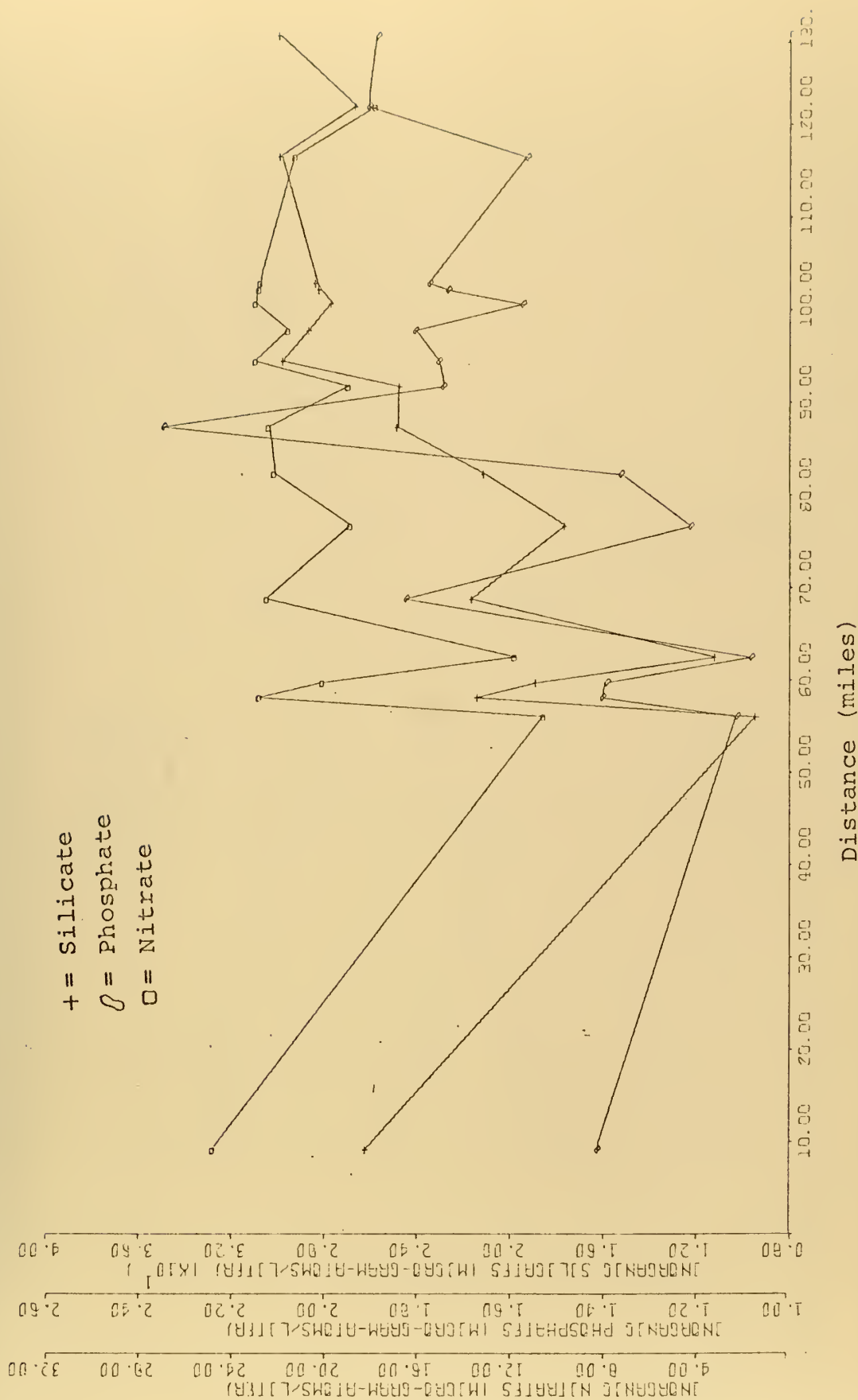


Figure 40. Nutrient Concentrations Versus Distance - Cruise #4 60 Meters Depth.

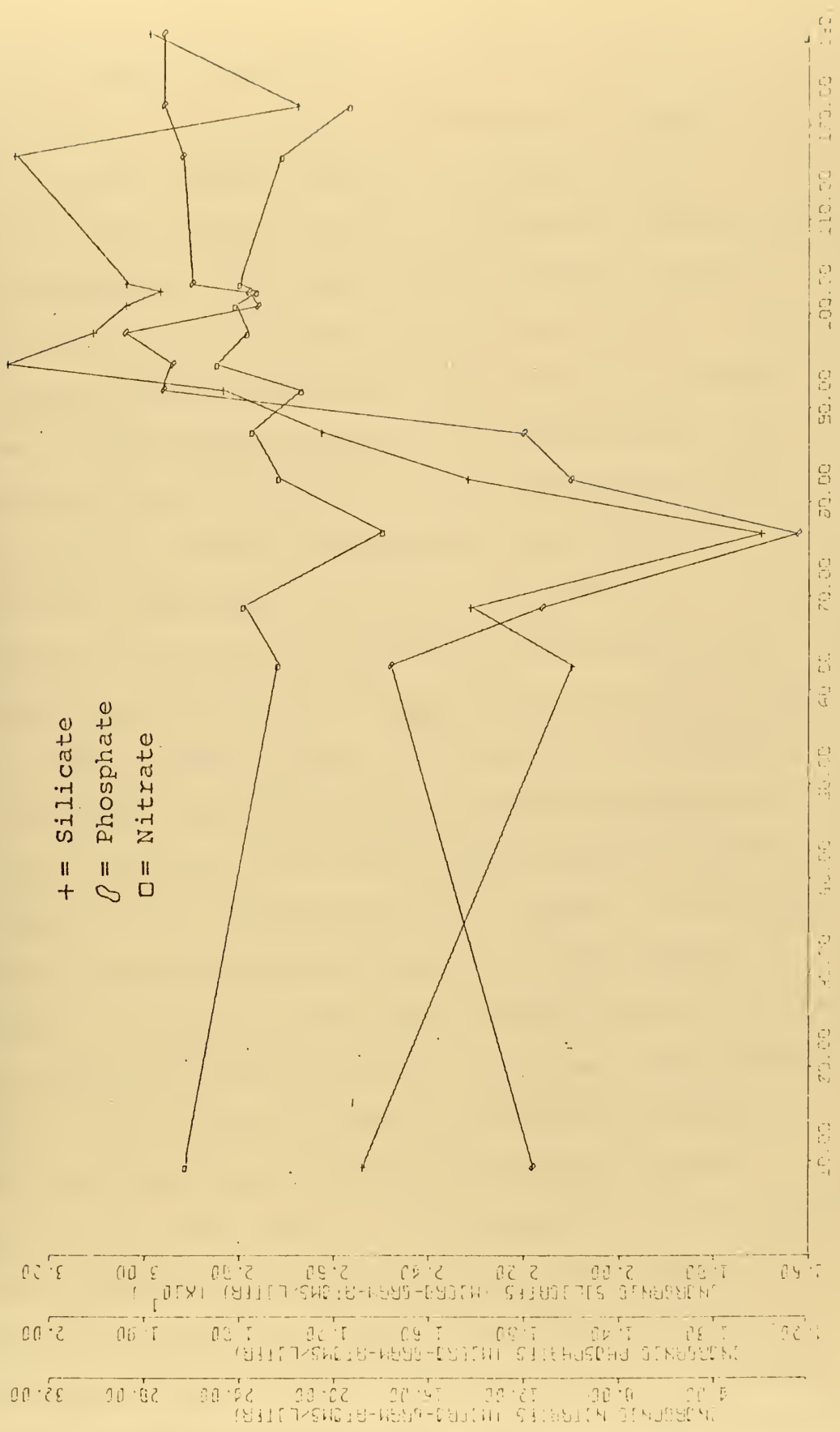


Figure 41. Nutrient Concentrations Versus Distance - Cruise #470 Meters Depth.

C. VERTICAL PROFILE VARIATIONS

Figures 42 to 52 illustrate representative results of vertical nutrient profiles found during cruise four.

Figure 42 is the profile found in 100 fathoms of water during leg one (Station 3). This represents a "normal" profile where the three major nutrients are well correlated, essentially constant through the mixed layer (depth 40 meters) then show a rapid increase through the thermocline. The major nutrients show a gradual increase with depth below the thermocline. Nitrite concentration indicates the reverse effect, decreasing through the thermocline.

Figure 43 is a vertical profile of the nutrient concentrations representative of the profiles obtained in the nutrient plateau areas of legs three and four (Stations 2, 3, 4). In these areas the nutrient concentrations were found to be relatively high and constant from the surface to the depth of the thermocline (40-50 meters). Across the thermocline the concentrations increased significantly.

Figure 44 illustrates the type profiles obtained in the areas of plankton blooms along legs three and four (Stations 1 and 5). This station was taken at 0140 in the morning and indicates the significant decrease in all nutrient concentrations in the upper 10 to 15 meters. The biological population appears to be very shallow and has driven the concentration levels down. The concentrations found below the planktonic layer (greater than 20 meters) is much like those found throughout the plateau region and indicates the same water mass.

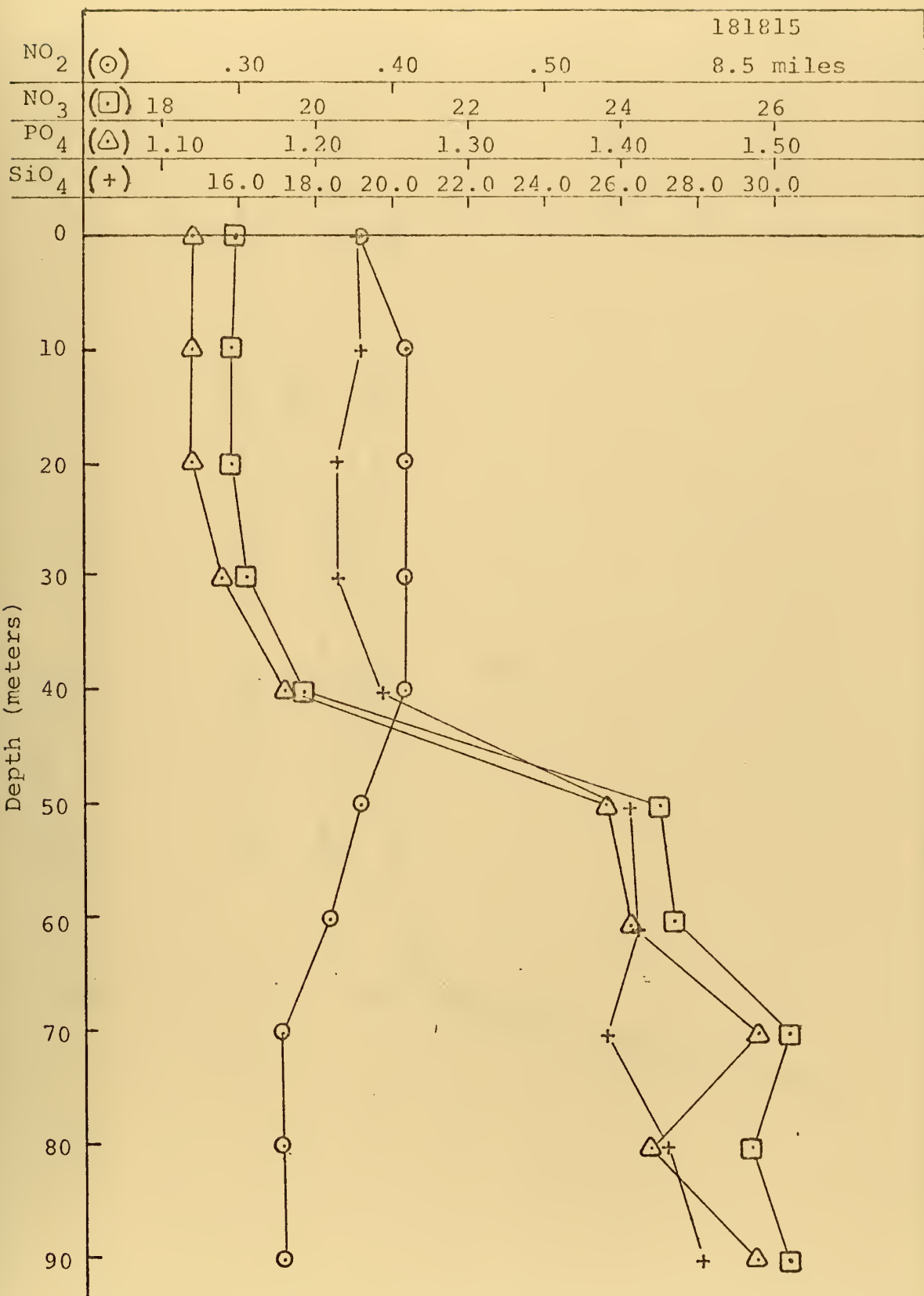


Figure 42. Vertical Profile Leg One Station 3.

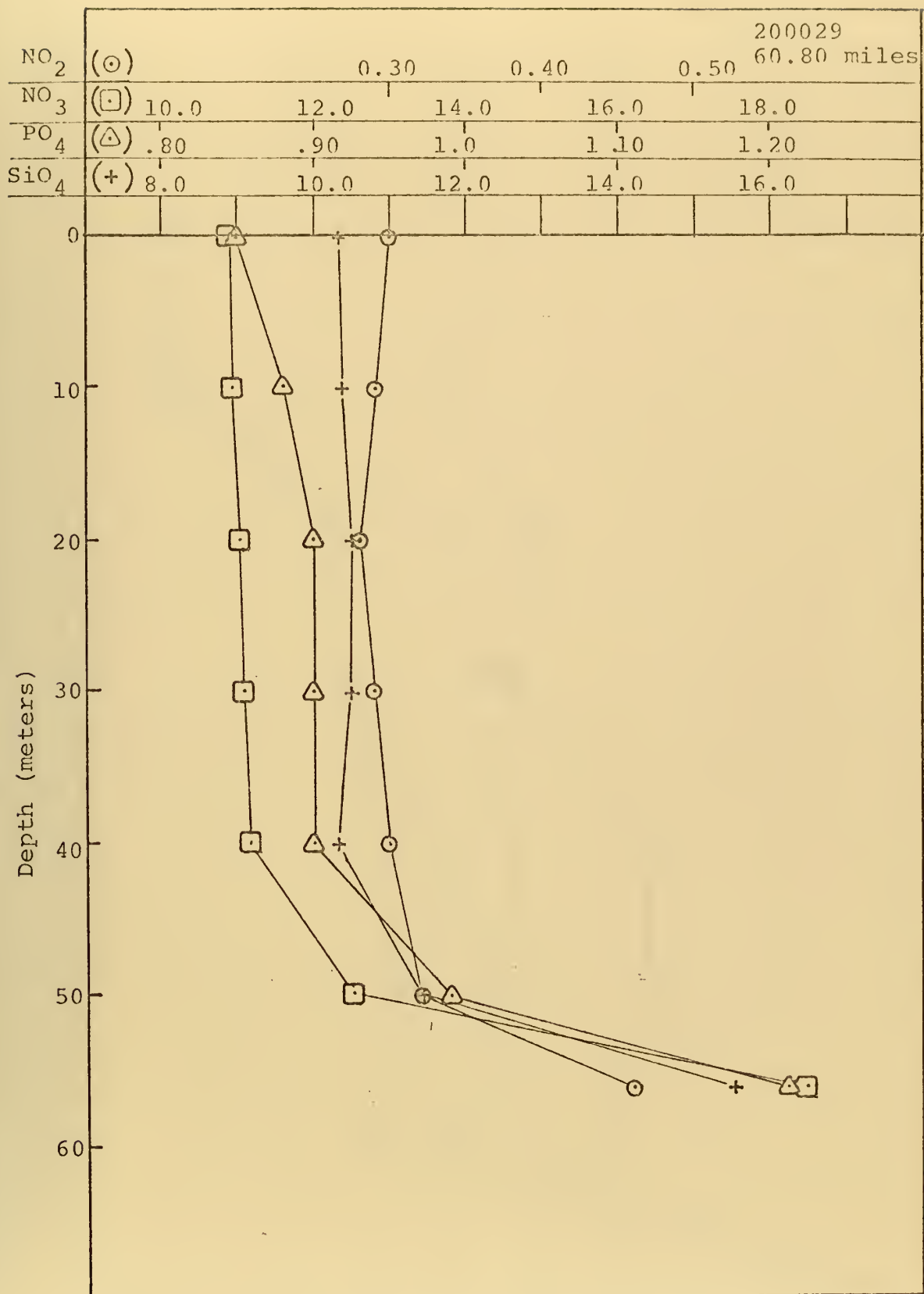


Figure 43. Vertical Profile Leg Four Station 4.

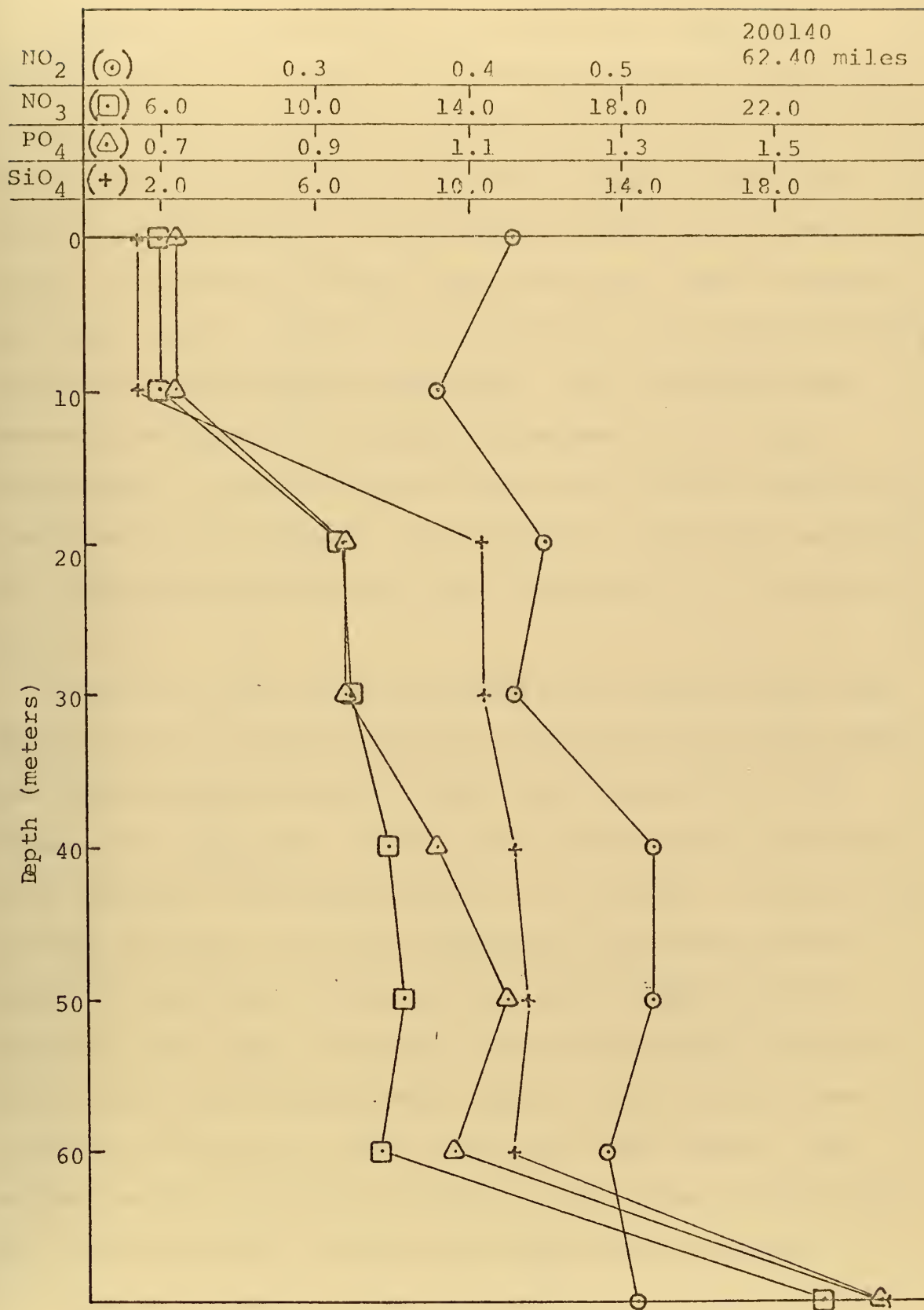


Figure 44. Vertical Profile Leg Four Station 5.

Figure 45 is the profile of station six (leg four) located close to the edge of a nutrient plateau (Figure 31). This station was sampled at sunrise and indicates a combined plateau-bloom activity. The surface concentrations were again near constant to 20 meters but having concentration values intermediate between those found for "pure" plateau and bloom areas. Between 20 and 45 meters the concentrations were again significantly depressed. This indicated the downward movement of biological organisms as the light intensified. Below 45 meters the profile values dramatically increased to the maximum values found on legs three and four. The temperature profile was near isothermal to 70 meters in this area.

Figure 46 is the vertical profile of station D-30, leg 5A (Figure 22). This profile was obtained three hours later and seven miles shoreward of the last (Figure 45). Two changes are important. First, the concentrations were even more depressed and extend from 10 to 40 meters. Second, the surface nutrient values had increased indicating physical effects (upwelling, currents) are mixing higher nutrient waters in the upper 10 meters. This station was the first where significant spikes were found in the surface values caused by sampling at zero versus 13.5 foot depths. The strong negative gradient observed in the upper 10 meters of the vertical profile explain the differences observed.

Figures 47 and 48 illustrate profiles of stations D-25 and D-20 (leg 5A, Figure 22). Station D-25 was located in

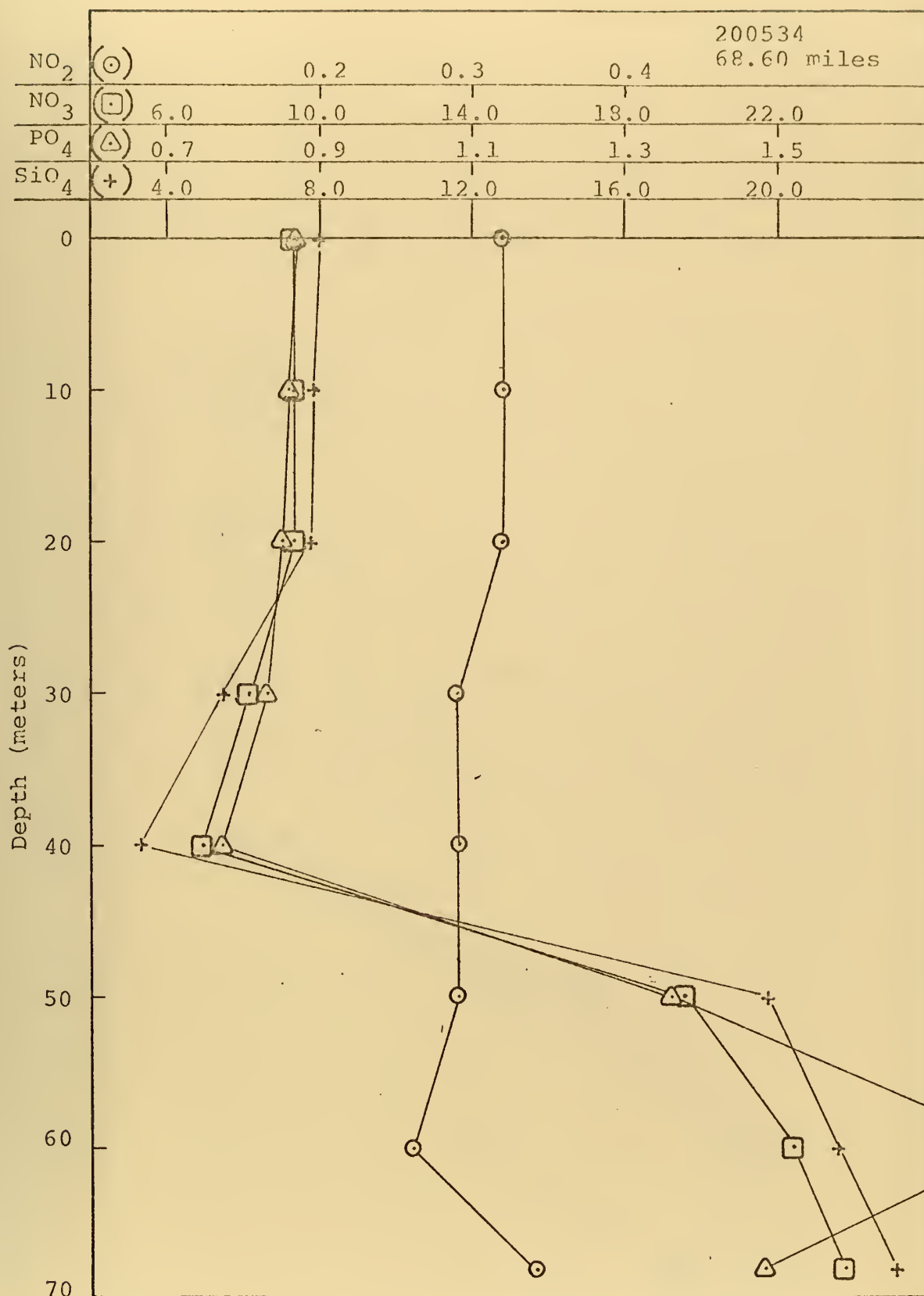


Figure 45. Vertical Profile Leg Four Station 6.

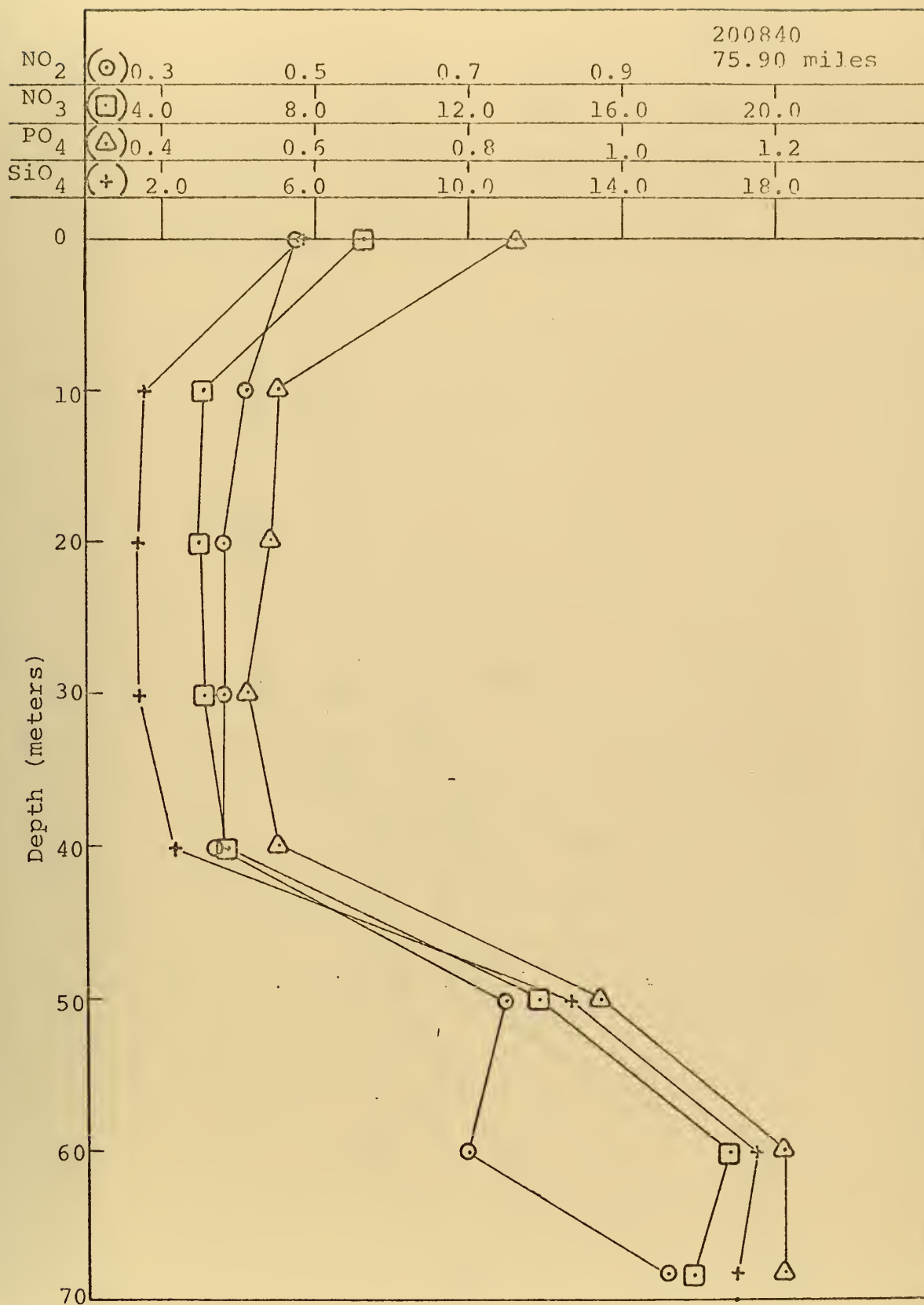


Figure 46. Vertical Profile Leg 5A Station D-30.

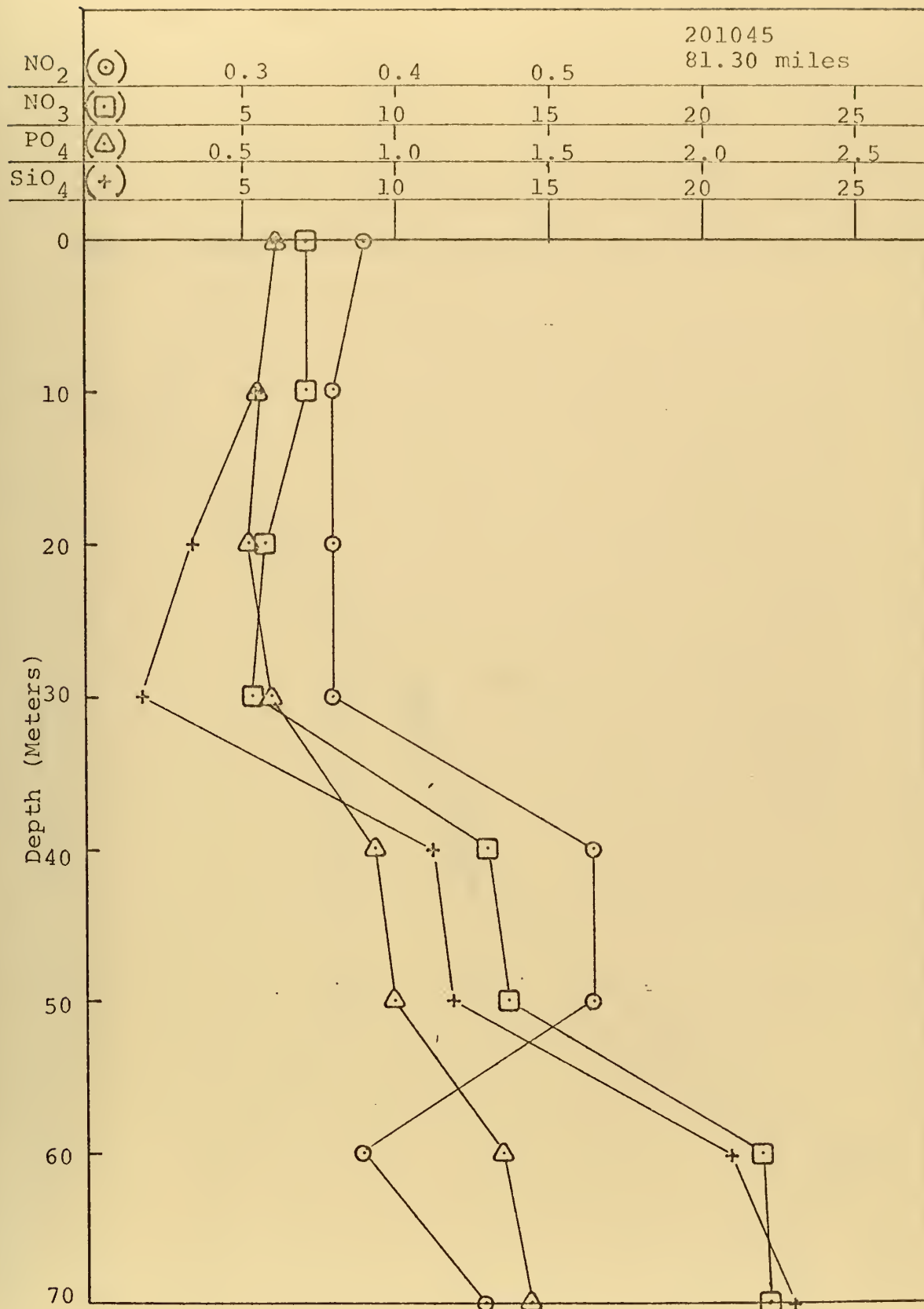


Figure 47. Vertical Profile Leg 5A Station D-25.

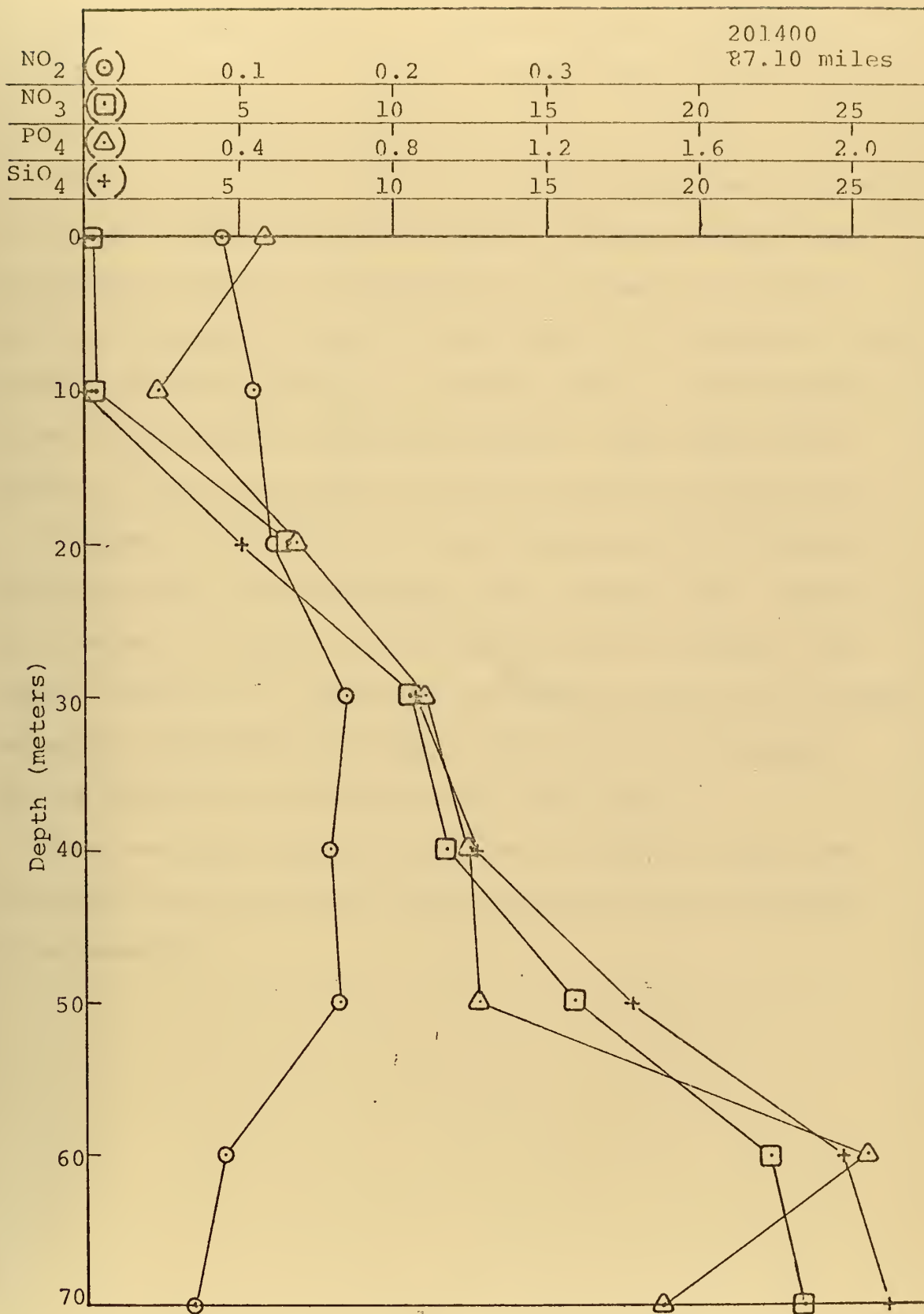


Figure 48. Vertical Profile Leg 5A Station D-20.

a nutrient plateau region. Station D-20 was located in a surface bloom area and closely follows those found in leg three and four blooms (Figure 44).

Figure 49 and 50 illustrate adjacent stations D-15 and D-12.5 (2.5 miles apart) (Figure 22). These stations were noticeably different, especially in the upper 30 meters. Again a depressed region is found from 10 to 20 meters for station D-15 but lacking in station D-12.5. The concentrations at all depths increased notably over those found farther to sea, indicating upwelling was more significant.

Figures 51 and 52 illustrate another pair of stations located in the leg 5B upwelling area (Figure 33). Station D-10 showed a strong positive concentration gradient with depth. Station D-7 indicated the common surface to 10 meter negative concentration gradient below which was found a strong increase in concentrations with depth.

The remaining vertical profiles had many of the same characteristics discussed above relating to the different areas sampled.

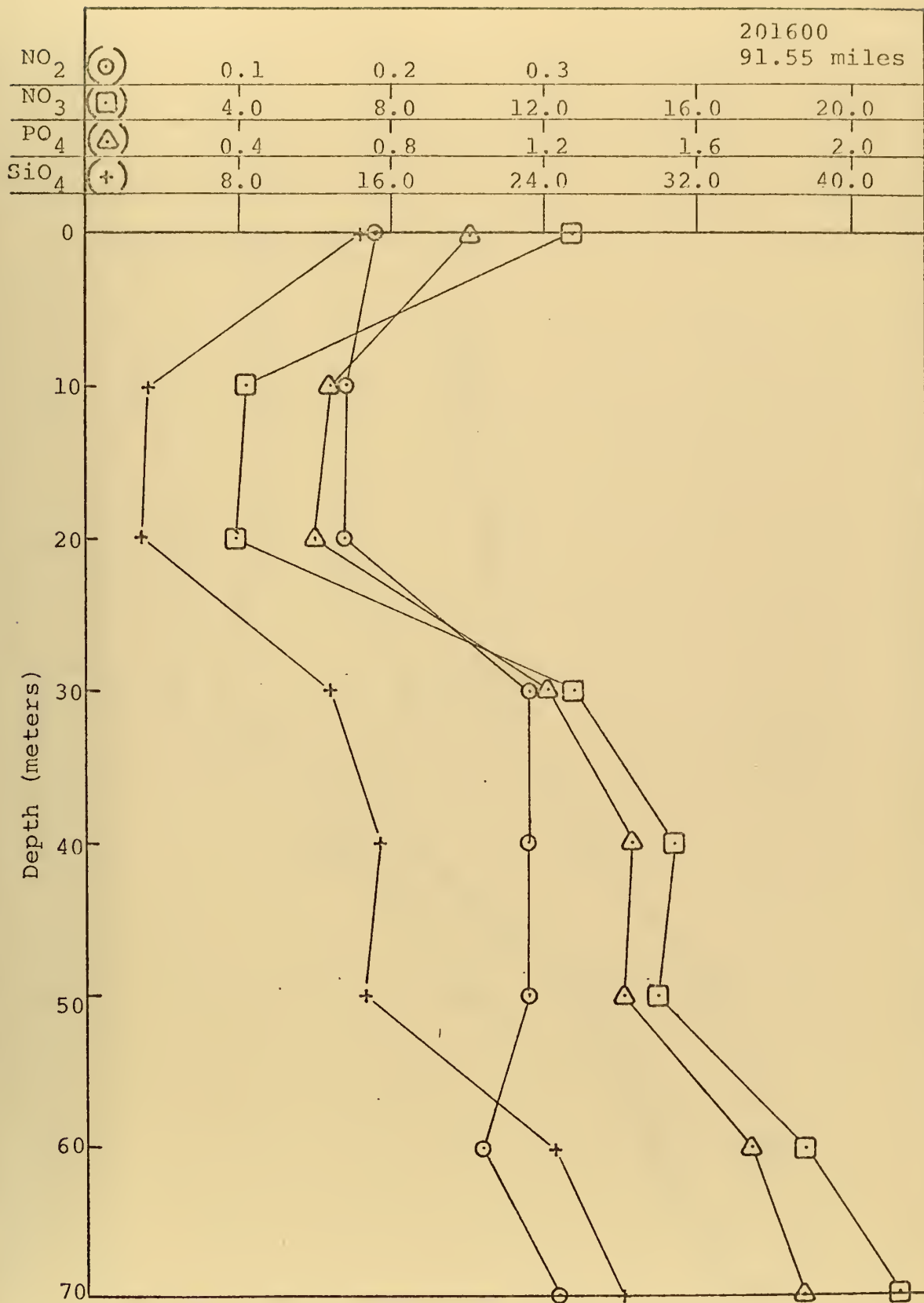


Figure 49. Vertical Profile Leg 5B Station D-15.

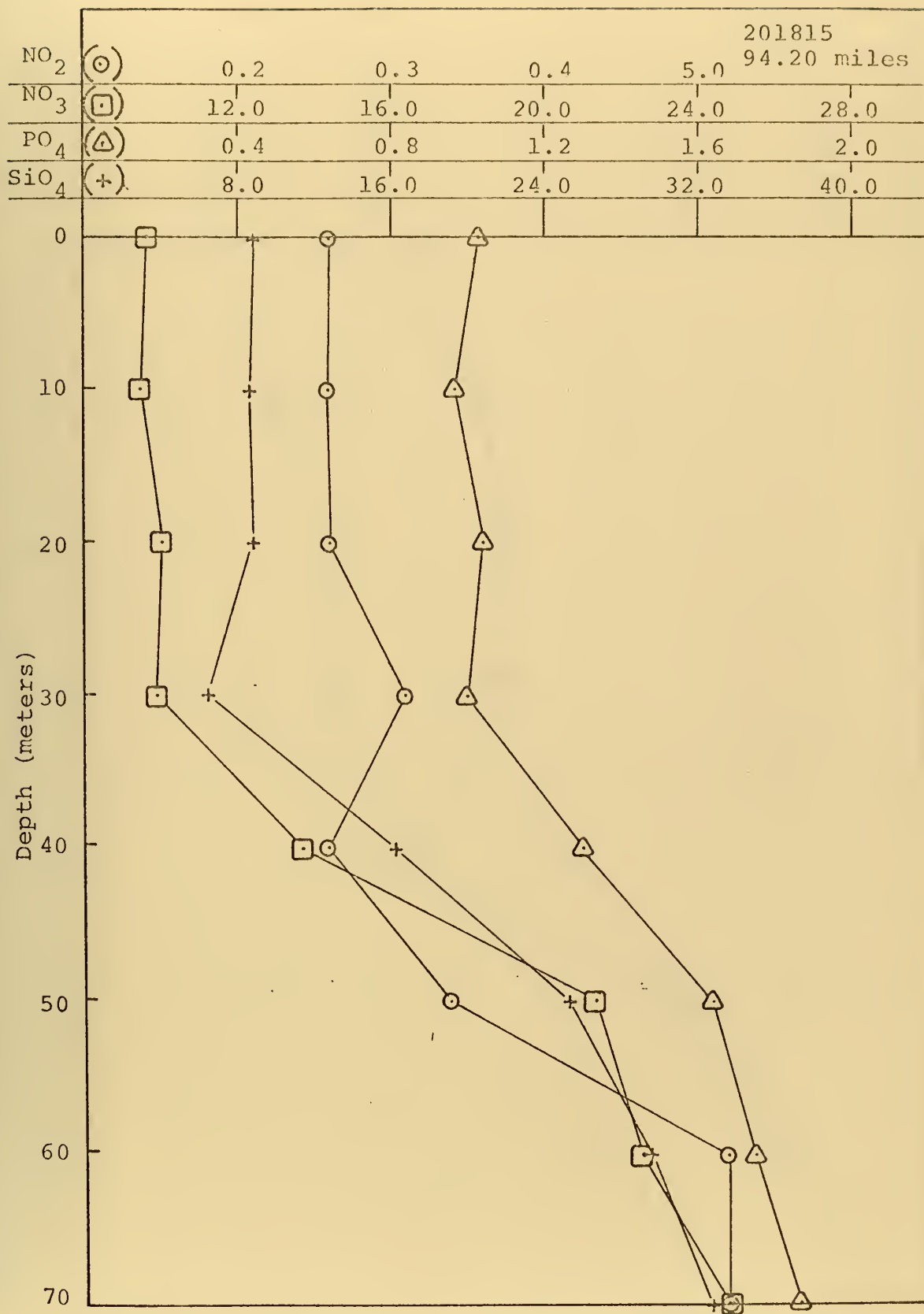


Figure 50. Vertical Profile Leg 5B Station D-12.5.

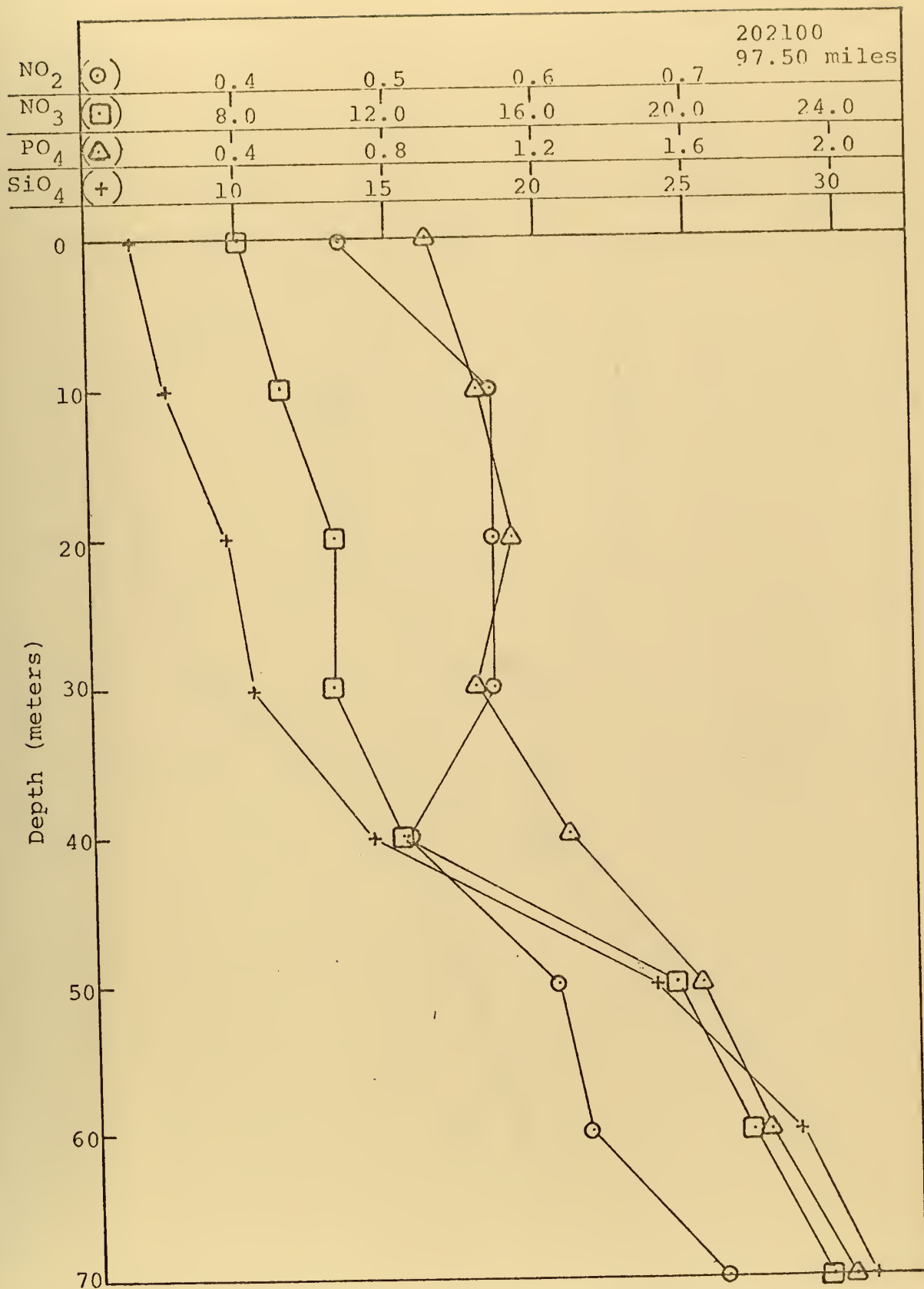


Figure 51. Vertical Profile Leg 5B Station D-10.

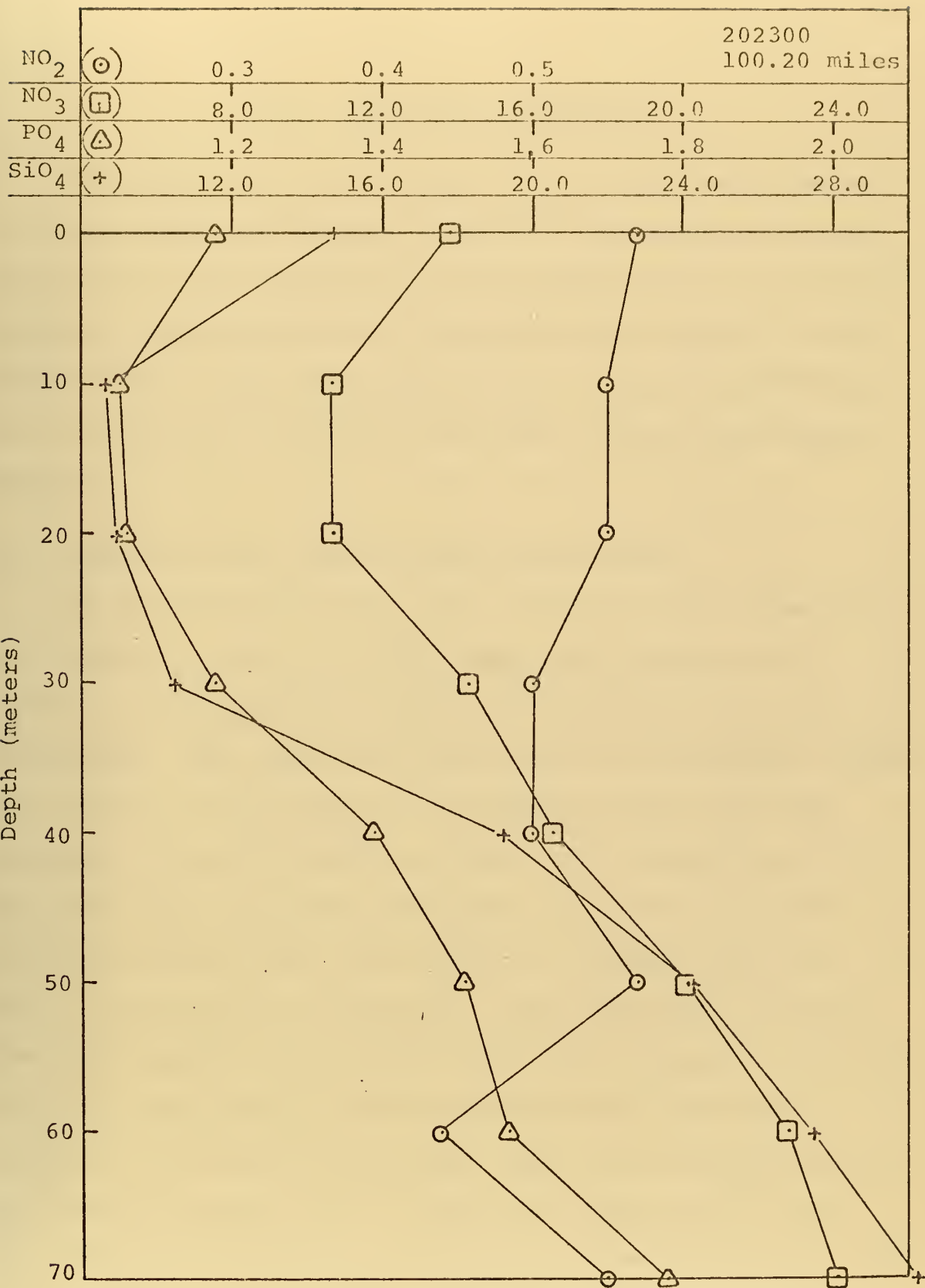


Figure 52. Vertical Profile Leg 5B Station D-7.

VII. DISCUSSION OF RESULTS

Some discussion was included with the data presentation of this study in an attempt to explain and clearly indicate meaningful results obtained. Further discussion is believed necessary to bring together the various areas and differing methods used in the data presentation. Also, some development is desirable to explain the major nutrient variations found.

A. VARIABILITY AND CONCENTRATION CORRELATIONS

All data obtained during this study have been presented. No attempt was made to discard any results because they didn't fit a particular criterion or correlate with surrounding values. One sample point was thrown out, however, because one nutrient value indicated contamination and drove the recorder off scale (estimated 130%). The correlations of the three major nutrients throughout this study indicated extremely close effects from physical (mixing, upwelling, etc.) and biological influences. This result was expected for the phosphate and nitrate variations but was not expected to be as close for the silicate variations influenced by differing biological mechanisms. The nitrite variations did not change directly with the other nutrients but did show an indirect relationship with nitrate concentrations in areas of high biological activity. This result was expected.

All major nutrients in the surface waters and the mixed layer varied over a wide range of concentrations for the area and times studied. Table V indicates the max-min values obtained from this study. As the results presented clearly indicate, not only do the concentrations vary greatly, but change significantly in small horizontal distances and vertical depths. It is obvious that data obtained from relatively widely spaced stations and taken at intervals from weeks to years can not be used for meaningful comparisons or as an accurate indication of water type in the photic zone of the oceans.

TABLE V
MAXIMUM-MINIMUM NUTRIENT CONCENTRATIONS
FOUND IN THE PHOTIC ZONE ($\mu\text{g/l}$)

	SILICATE		PHOSPHATE		NITRATE	
	MAX	MIN	MAX	MIN	MAX	MIN
Surface	32.63	0.0	1.72	0.14	24.18	0.0
Subsurface	34.21	0.0	2.34	0.19	26.21	0.36

B. UPWELLING SIGNATURES

Three upwelling area signatures have been obtained and discussed (Figures 25, 29, and 33). The last (Figure 33) was investigated more thoroughly than the others. A vertical contour plot of isolines of equal silicate concentration

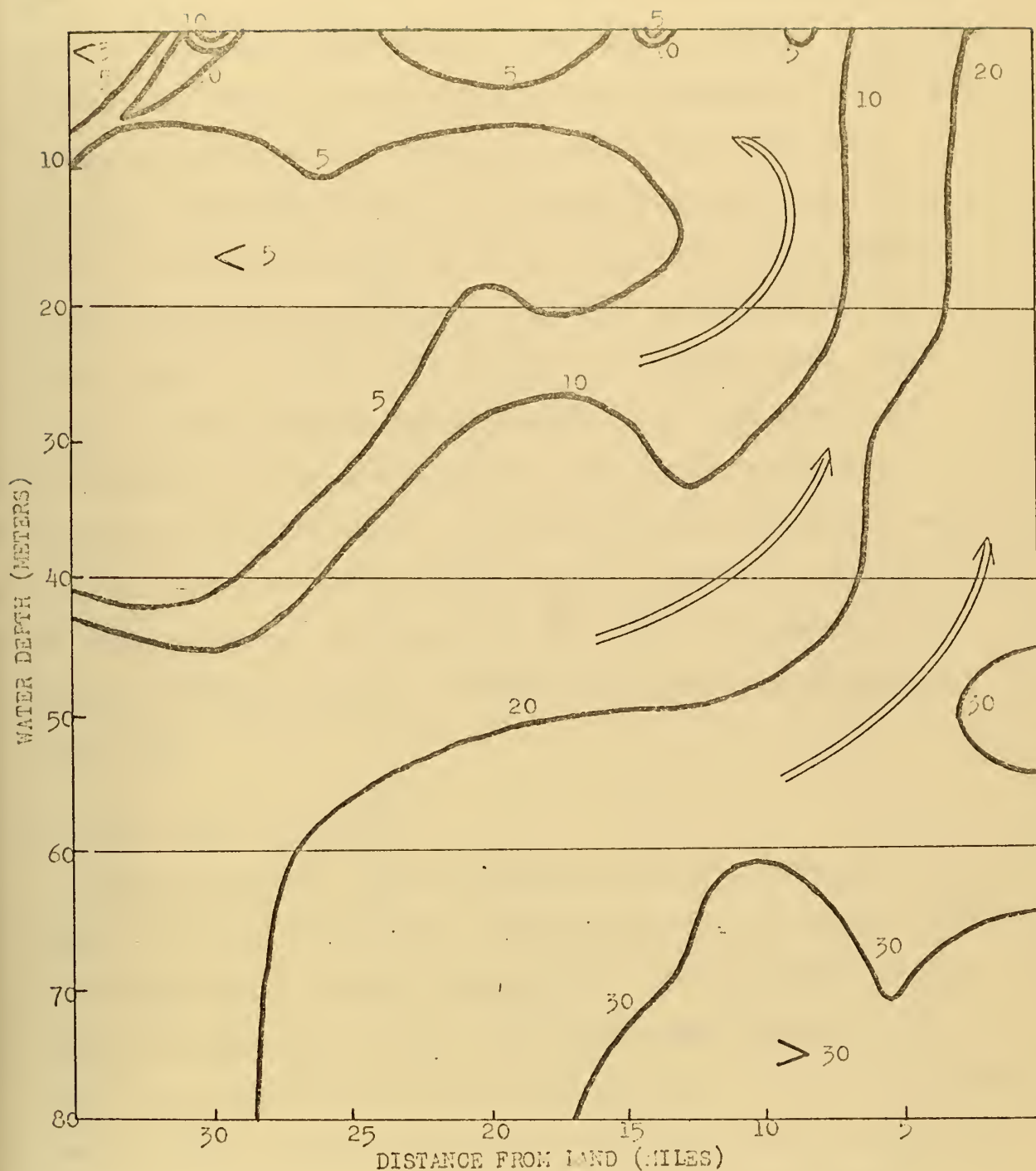


Figure 53. Vertical Contour Plot of Silicate Isolines in Upwelling Area Leg 5B.

along legs three and four (Figures 30 and 31) of cruise four. The results as presented are difficult to understand because of a complicated ship track in that area. Figure 54 illustrates the limits of the bloom/plateau boundaries along the track as discussed for legs three and four. The data obtained represents only two plateau regions. The larger region contains stations 2, 3, 4, and 6 while the smaller region encloses no stations. Stations one and five are close together outside the plateau in a bloom area. The limits of the plateau regions parallel to the track are estimated from the dimensions of the actual boundaries obtained along the track. The axis of the plateaus closely parallels the submarine canyon valley and may be indicative of vertical water motions from the canyon maintaining the nutrient surface levels. Further data must be obtained in this area.

D. BAY AREA VARIATIONS

Three Monterey Bay area signatures were obtained; cruise three (Figures 26 and 27), cruise four leg one (Figure 28) and cruise four leg six (Figure 34). These surface signatures significantly differ from each other although they were along much of the same track location. This indicates the variation in data obtained when sampling at intervals of a few days or weeks. Cruise three data, as discussed earlier, were highly variable with a significant plateau developing in the outer area. Cruise four data showed a more constant distribution over the Monterey Canyon. This

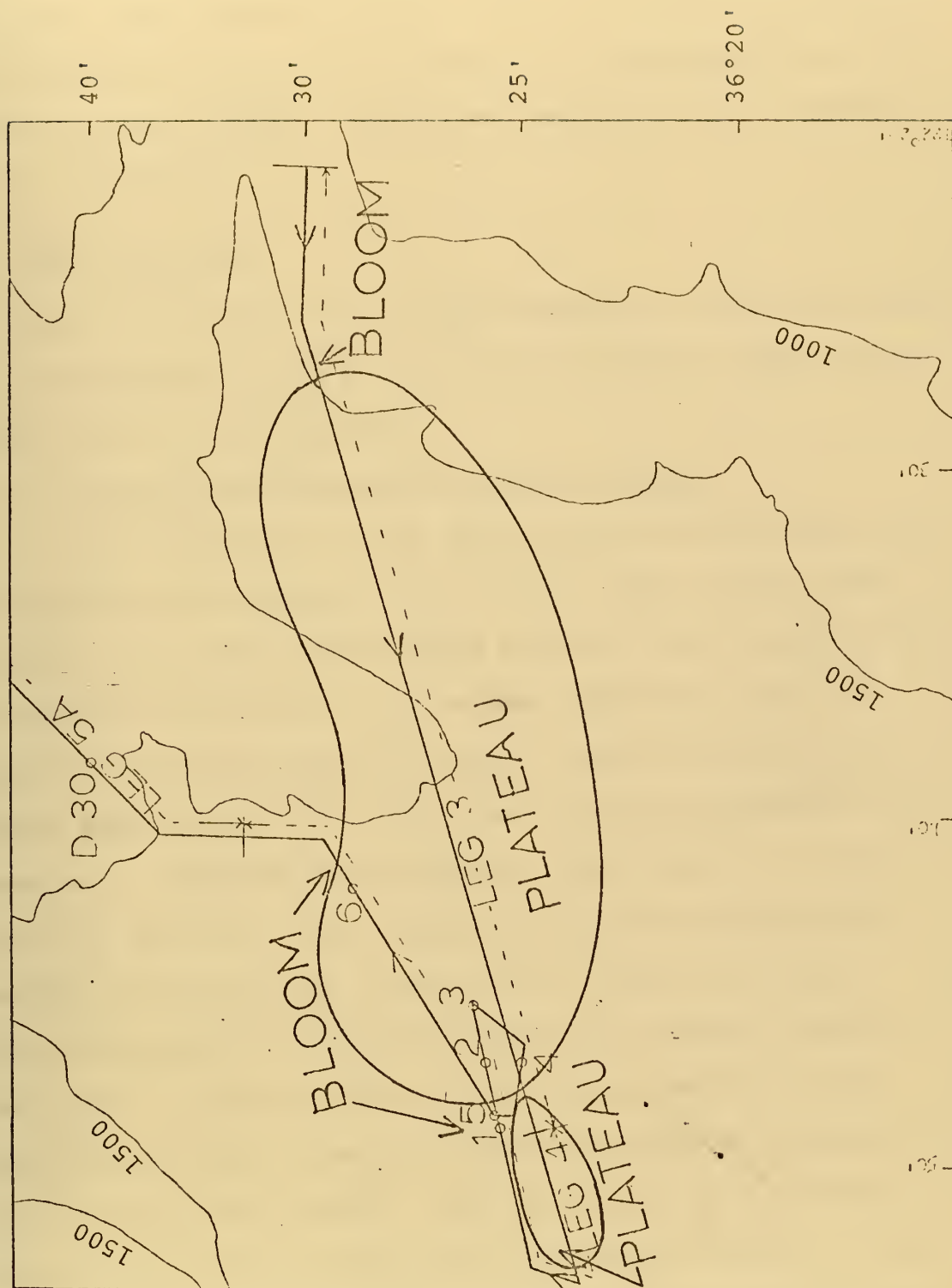


Figure 54. Bloom/Plateau Boundaries Found During Legs Three and Four.

may have been caused by either intensification of circulation above the canyon or a reduction in biological activity in the surface waters. Data were insufficient to confirm either condition.

E. RATIO ANALYSIS

Nutrient ratios for Silicate:Phosphate, Silicate:Nitrate, Nitrate:Phosphate, and Total Nitrate:Phosphate were calculated for all data obtained.

1. Area Identification by Surface Ratios

An evaluation of the calculated surface ratios was attempted to determine if the surface ratio values would identify the water masses found earlier from concentration distribution patterns. All ratios associated with the earlier upwelling plateau regions, open sea nutrient plateaus, planktonic bloom areas, and Bay area plateaus were separated, analysed, and averaged. The results are indicated in Table VI. The differences between maximum and minimum values for all ratios and all areas are quite significant and do not show particularly constant results throughout a specific area. The average values for the determined ratios, however, do seem to be more representative of the water masses. The values for the specified areas of interest do show some interesting results. The highest surface nutrient concentrations were found in the strongest upwelling areas and generally decreased seaward. The nutrient ratios, however, for the upwelled areas were

Table VI. SURFACE NUTRIENT RATIOS

Area Description	Distance (Fm - To)	SiO ₄ /PO ₄		SiO ₄ /NO ₃		NO ₃ /PO ₄		Total NO ₃ /PO ₄					
		Max	Min	Ave	Max	Min	Ave	Max	Min				
<u>UPWELLING PLATEAUS</u>													
C2 (7) *	3.00-10.00	13.74	12.13	12.99	1.31	1.19	1.24	10.78	10.18	10.46	10.99	10.40	10.70
C4-LEG 2 (11)	4.20-15.60	13.65	10.74	12.58	1.06	0.90	0.99	13.68	11.65	12.74	13.92	11.91	13.02
C4-LEG5B (36)	94.0-105.4	19.99	4.78	10.59	1.71	0.56	0.96	14.06	5.89	10.74	14.26	6.12	11.10
<u>OPEN SEA NUTRIENT PLATEAUS</u>													
C4-LEG 3(19)	31.0-45.0	12.33	8.91	10.18	1.02	0.84	0.92	12.31	10.51	11.09	12.83	11.09	11.65
C4-LEG 4(11)	47.0-51.0	10.13	8.46	9.42	0.98	0.79	0.90	11.88	9.70	10.48	12.56	10.32	11.12
C4-LEG 4(8)	57.3-61.0	13.53	10.94	11.76	0.97	0.95	0.96	14.23	11.51	12.29	14.63	11.88	12.68
C4-LEG 4(25)	62.9-70.0	13.13	6.35	10.46	0.97	0.62	0.90	13.72	9.85	11.59	14.22	10.20	12.01
C4-LEG 5(11)	75.9-84.0	10.65	4.25	8.49	0.90	0.40	0.73	12.41	10.50	10.46	12.91	11.07	12.12
<u>OPEN SEA BLOOMS</u>													
C4-LEG 2(8)	18.0-26.5	0.00	0.00	0.00	0.00	0.00	0.00	6.23	0.00	1.91	6.96	1.22	3.05
C4-LEG 3(4)	45.9-47.0	0.35	0.00	0.09	0.05	0.00	0.01	7.10	0.59	4.03	7.89	1.61	4.96
C4-LEG 4(7)	51.0-56.0	0.00	0.00	0.00	0.00	0.00	0.00	2.13	0.87	1.26	3.24	1.92	2.55
C4-LEG 5(4)	72.4-75.4	0.00	0.00	0.00	0.00	0.00	0.00	8.51	4.05	6.08	9.18	4.41	6.71
C4-LEG 5(9)	85.0-90.5	2.18	0.00	0.24	0.47	0.00	0.05	5.41	0.06	1.87	6.30	0.28	2.27

BAY AREA PLATEAUS

C3 (9)	8.50-12.10	16.17	14.94	15.30	1.36	1.31	1.34	12.00	11.15	11.42	12.34	11.45	11.73
C4-LEG 1(21)	7.00-20.00	18.24	15.90	17.02	1.04	0.90	0.98	18.21	16.76	17.38	18.43	17.12	17.65
C4-LEG 6(18)	109.0-122.0	16.83	9.37	12.71	1.32	0.90	1.18	13.04	8.21	10.80	13.33	8.47	11.06

* C signifies cruise (ie. Cruise 2)
() number of samples averaged

stantly different from the open sea plateau
this forces the conclusion that the change in
concentration was from circulation and mixing
nutrient ocean waters, resulting in a dilution
reduced the concentrations but maintained
proportions. The ratios determined from open
areas were drastically different from the others.
ratios ($\text{SiO}_4:\text{PO}_4$ and $\text{SiO}_4:\text{NO}_3$) had been depressed
but the $\text{NO}_3:\text{PO}_4$ and Total $\text{NO}_3:\text{PO}_4$ ratios,
smaller than before, were still significant. This
is that for these areas studied the silicate is
a nutrient for the biological population. This
is generally recognized [Riley and Skirrow 1965].
the plateau ratios appear to show significantly
less than those found in the other nutrient plateau
this effect may be partially caused by a greater
dilution due to river runoff into the Bay.

Twenty Meter Ratio Stability

nutrients have been used by some investigators
[Chow and Mantyla 1965] as a quasiconservative
enabling them to identify intermediate and deep
waters. Apparent oxygen utilization and deep ocean
nutrient concentrations have been found to be related
[Land and Kester 1966]. The assumption is made that
the nutrients found just below the photic layer
in the mixed layer consists of preformed nutrients
(is zero). These values are believed to be quite

Table VIII. Ratios of Nutrient Changes From 70 Meters Depth
to the Surface (Cruise Four)

Distance	ΔSiO_4	ΔPO_4	ΔNO_3	ΔNO_2	$\Delta\text{SiO}_4/\Delta\text{PO}_4$	$\Delta\text{SiO}_4/\Delta\text{NO}_3$	$\Delta\text{NO}_3/\Delta\text{PO}_4$	$\Delta\text{NO}_3\text{ Total}/\Delta\text{PO}_4$
9.29	5.64	0.32	6.38	-0.10	17.63	0.88	19.94	19.63
62.40	19.57	0.92	16.29	0.08	21.27	1.20	17.71	17.79
68.60	15.07	0.61	14.34	0.02	24.70	1.05	23.51	23.54
76.60	11.26	0.35	8.79	0.48	32.17	1.28	25.11	26.49
82.20	17.99	0.85	15.22	0.17	21.16	1.18	17.91	18.11
87.10	26.22	1.03	23.11	-0.02	25.46	1.13	22.44	22.42
91.55	13.89	0.80	8.54	0.12	17.36	1.63	10.68	10.83
94.20	23.98	0.84	15.26	0.26	28.55	1.57	18.17	18.48
97.50	23.90	0.98	14.20	0.09	24.39	1.68	14.49	14.58
100.45	21.51	0.72	13.26	0.13	29.88	1.62	18.42	18.60
101.90	19.17	0.70	11.55	0.10	27.39	1.66	16.50	16.64
102.70	16.51	0.67	10.10	0.05	24.64	1.63	15.07	15.15
116.25	22.88	0.96	12.34	0.07	23.83	1.85	12.85	12.93
121.60	8.63	0.59	5.52	0.00	14.63	1.56	9.36	9.36

the data are somewhat limited and do show some spread, the results (Table IX) appear significant. The average values obtained for $\Delta\text{NO}_3 : \Delta\text{PO}_4$ and $\Delta\text{Total NO}_3 : \Delta\text{PO}_4$ of 16.33 and 16.46, respectively, are in close agreement with the 16 : 1 ratio given by Fleming [1940] for average plankton. This value was also confirmed by Grill and Richards [1964] in laboratory studies of decomposing phytoplankton. The average value obtained for $\Delta\text{SiO}_4 : \Delta\text{PO}_4$ was 21.14. This is much different from the value of 16.00 suggested by Richards [1958]. It does agree very well with the $\Delta\text{SiO}_4 : \Delta\text{PO}_4$ ratio of 23:1 obtained in laboratory decomposition studies [Grill and Richards 1964]. Figures 55 and 56 are correlation diagrams of Table IX data. The high value of SiO_4/PO_4 assimilation ratio is again an indication of silicate as the limiting nutrient. In no samples tested was the SiO_4/PO_4 ratio this high. The NO_3/PO_4 assimilation ratio determined from Table IX is close to that found in the 70 meter samples (Table VII). Additional data and further studies in this area are considered promising.

F. TIME VARIATION STUDY

One additional result of this study must be included. During the period at anchorage outside Monterey Harbor on 19 May 1972, surface samples were taken at 10 minute intervals for four hours. The results of these time variations are indicated in Figure 57. Although the variations were small, the nutrients do seem to correlate quite well

Table IX. Ratios of Nutrient Changes From 70 Meters Depth
To The Nutrient Minimum (Cruise Four)

Distance	ΔSiO_4	ΔPO_4	ΔNO_3	ΔNO_2	$\Delta\text{SiO}_4/\Delta\text{PO}_4$	$\Delta\text{SiO}_4/\Delta\text{NO}_3$	$\Delta\text{NO}_3/\Delta\text{PO}_4$	$\Delta\text{NO}_3\text{ Total}/\Delta\text{PO}_4$
9.29	7.06	0.37	7.31	-0.08	19.08	0.97	19.76	19.54
56.00 *	9.38	0.85	9.93	0.21	11.04	0.94	11.68	11.94
58.00 *	10.83	0.51	11.77	0.07	21.24	0.92	23.08	23.22
59.60 *	8.75	0.50	9.29	-0.01	17.50	0.94	18.58	18.56
60.80 *	1.13	0.14	1.61	0.02	8.07	0.70	11.50	11.64
62.40	19.57	0.92	16.29	0.13	21.27	1.20	17.71	17.85
68.60	19.75	0.71	16.84	0.05	27.82	1.17	23.72	23.79
76.60	15.60	0.70	12.88	0.58	22.29	1.21	18.40	19.23
82.20	21.37	0.93	16.90	0.10	22.98	1.26	18.17	18.28
87.10	26.22	2.15	23.12	-0.05	12.20	1.13	10.75	10.73
91.55	25.26	1.28	17.40	0.14	19.73	1.45	13.59	13.70
94.20	26.37	0.90	15.34	0.26	29.30	1.72	17.04	17.33
97.50	24.45	1.01	15.53	0.25	24.21	1.57	15.38	15.62
100.45	21.68	0.73	13.44	0.00	29.70	1.61	18.41	18.41
101.90	18.89	0.68	11.45	0.10	27.78	1.65	16.84	16.99
102.70	16.51	0.67	10.15	0.05	24.64	1.63	15.15	15.22
116.25	20.98	0.78	11.56	0.00	26.90	1.81	14.82	14.82
121.60	8.76	0.59	5.52	0.00	14.85	1.59	9.36	9.36
AVERAGE					21.14	1.30	16.33	16.46

* Values From Maximum Depth Sampled (60 Meters)

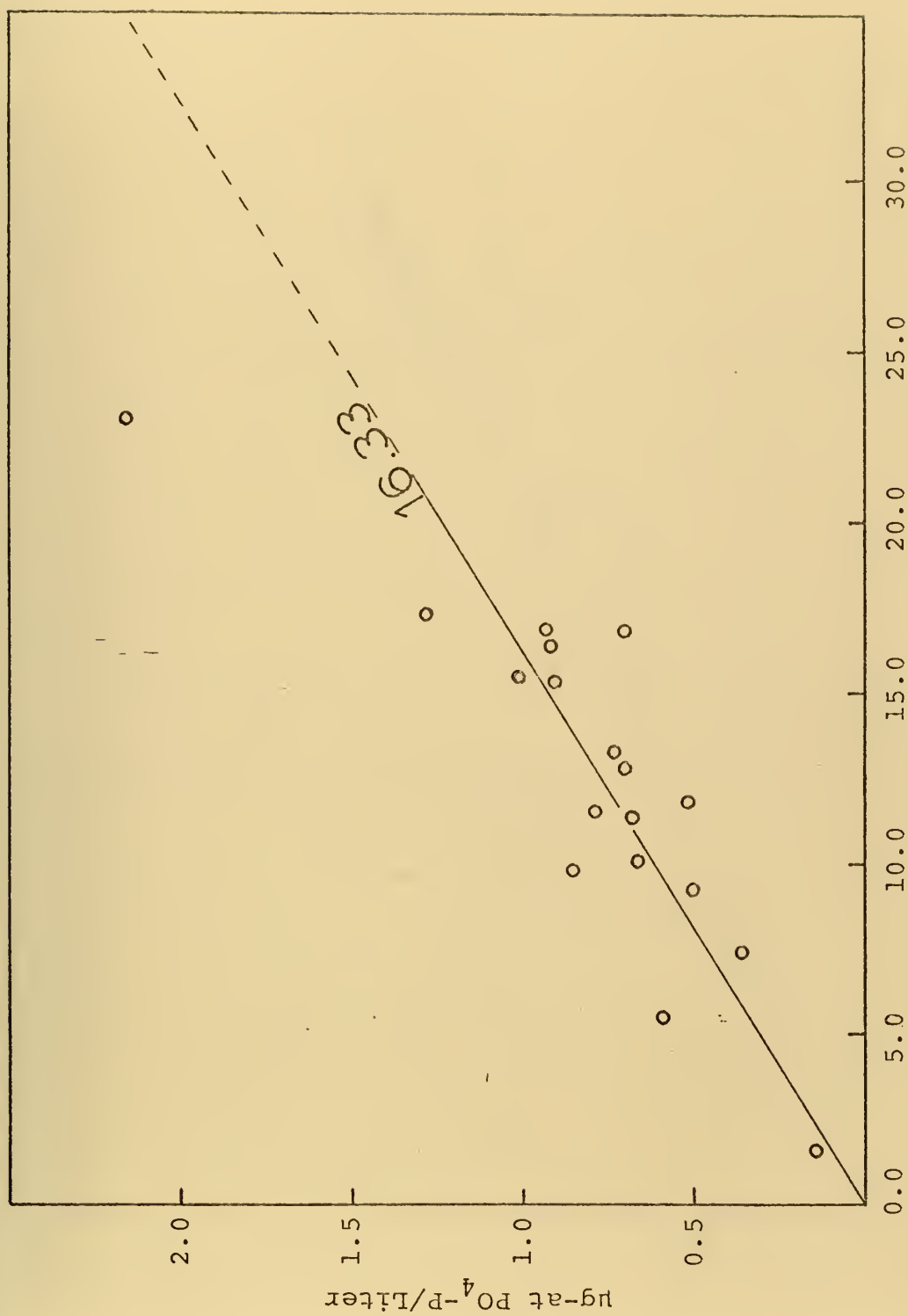


Figure 55. Correlation Diagram of the Nitrate/Phosphate Assimilation Relationship.

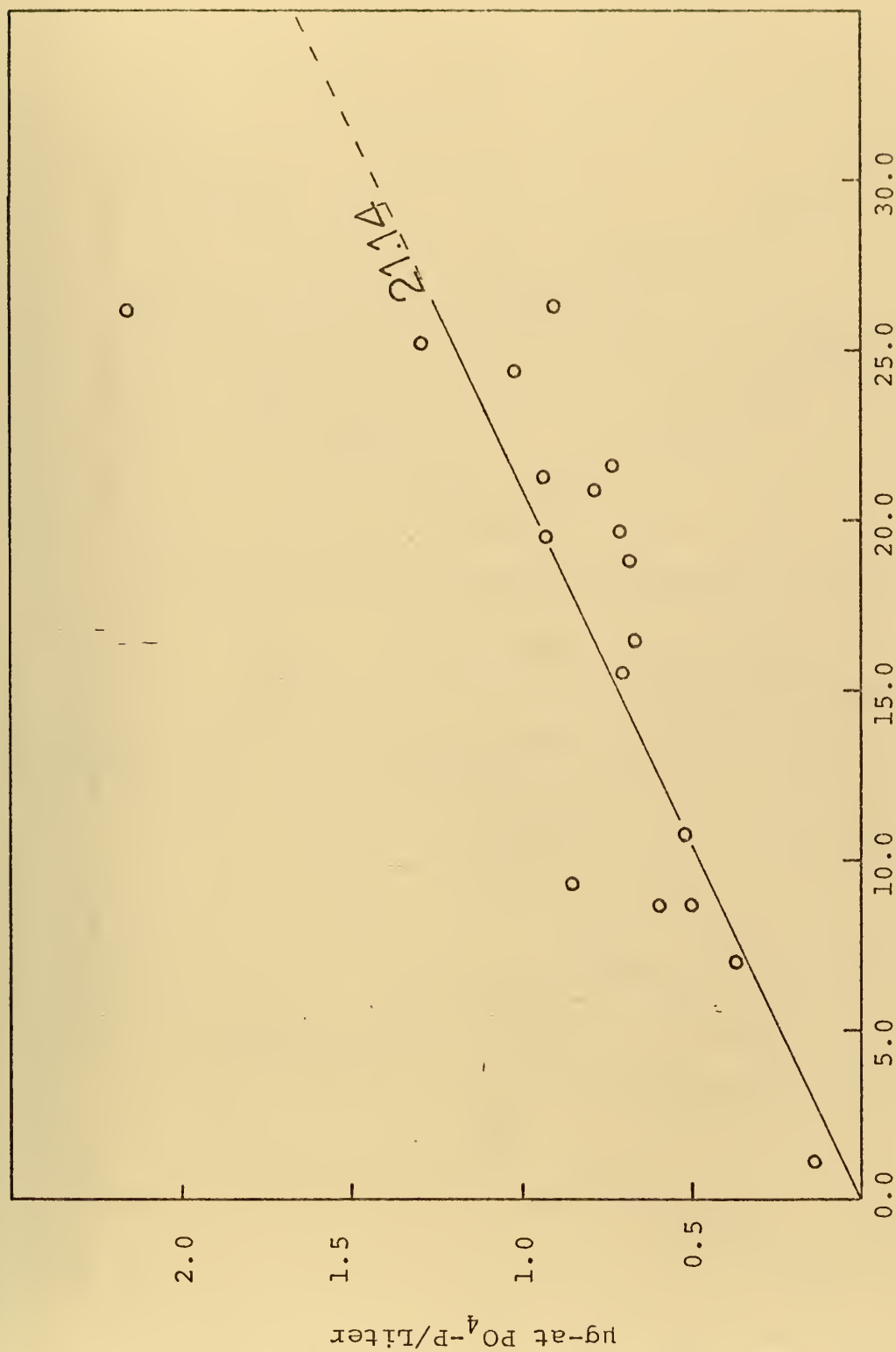


Figure 56. Correlation Diagram of the Silicate/Phosphate Assimilation Relationship.

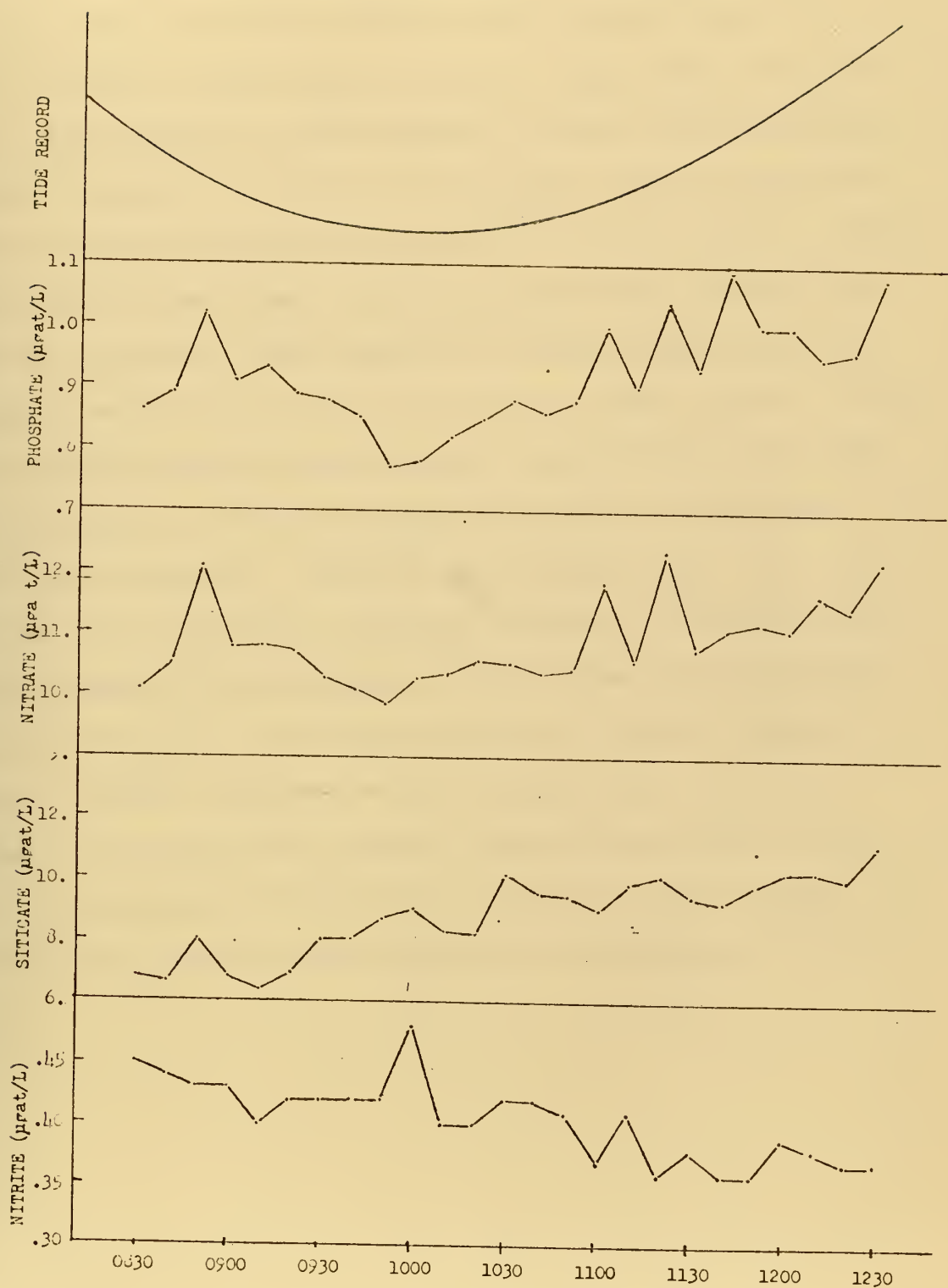


Figure 57. Surface Nutrient Time Variations 19 May 1972.

and indicate the sensitivity of the analytical techniques. The tide record is shown for this time period.

Phosphate and nitrate concentration levels appear to have a minimum at time 0950. This was also the time of low tide. Superimposed on the apparent nutrient tidal changes are oscillations. Phosphate and nitrate show oscillations with a 20 minute period over about 40% of the record. These oscillations appear real and may be caused by langmuir circulation [Langmuir 1938] patterns in the surface waters as the water mass moved by the ship in the tidal current. This would explain why the oscillations stopped during the time of low tide when outflow stopped and before significant inflow had developed. Nitrite and silicate data also show an oscillation tendency (silicate period of 40 minutes and nitrite period of 20 minutes). Insufficient data prevents further evaluation but these suggest an area for further study. Results indicate nutrient variations caused by surface circulation and internal wave motions may be determined by sampling at closer time intervals (1-2 minutes) or continuously without wash separation [Armstrong and LaFond 1966].

VIII. SUMMARY AND CONCLUSIONS

This study has demonstrated the capabilities of the Technicon[®] AutoAnalyzer[®] II System. The sensitivity, reproducibility, and accuracy of this system for sea water nutrient analysis have been found to be very satisfactory. The system was capable of operating at sea, even under adverse weather conditions, and accurate, meaningful data were obtained.

Results obtained were examined in light of the many areas of biological and physical oceanography which might be studied using these high resolution techniques. The high nutrient variations in the sampling area have been presented and explanations for them offered. Upwelling areas have been investigated for nutrient concentrations, circulation patterns, and variations in nutrient ratios. Planktonic bloom areas have been identified from the low nutrient levels, low nutrient ratio values and high chlorophyll correlations. Results indicate that silicate was the biological limiting nutrient in the waters studied. Vertical nutrient profiles have been presented for the areas studied. The biological and physical influences on these profiles have been discussed and separated. Assimilation ratios for biological activity of 16.33 for $\text{NO}_3:\text{PO}_4$ and 21.14 for $\text{SiO}_4:\text{PO}_4$ were obtained which agree well with laboratory decomposition values. Nutrient plateau regions have been analysed and sources

discussed. The major cause of nutrient concentration changes in the area (outside the blooms) studied appears to be mixing caused by circulation patterns which reduce the concentrations while maintaining nutrient ratios.

Areas of further investigation have been identified throughout this paper. Additional evaluation and improvements in sampling techniques, operating procedures, and data processing have been identified. Additional investigation in promising areas of mixed layer circulation and biological/physical relationships with nutrient variations have been indicated.

Three major conclusions have resulted from this study:

1. Satisfactory automated equipment exists which permits high resolution real-time study of oceanic processes which affect nutrient concentrations.

2. Among the environmental processes that may be studied are biological processes, mixing internal waves, tidal variations and circulation patterns such as Langmuir cells.

3. The possibility of real-time measurements should allow better field decisions when interesting phenomena are encountered.

APPENDIX A

SAMPLE DATA WORK SHEET

 PAGE 1
 CRUISE NO. 2
 DATE 4/28/72

SAMPLE #	TIME	DEPTH	%	B.L. CORR	STAND CORR	SALT CORR	CORR %	CONC	3.1 CORR	STAND CORR	SALT CORR	CORR %	CONC	4.1 CORR
1	1225	STD	48.1	0.0	100.0	50.0	—	—	—	—	—	—	—	—
2	1225	STD	60.1	0.08	—	50.18	—	—	—	—	—	—	—	—
3	1225	STD	12.7	0.17	—	12.87	—	—	—	—	—	—	—	—
4	1225	STD	98.3	0.25	—	98.58	—	—	—	—	—	—	—	—
5	1225	STD	—	—	—	—	—	40.0	0.0	—	—	40.0	10.0	—
6	1225	STD	—	—	—	—	—	40.1	0.02	—	—	40.12	10.0	—
7	1225	STD	—	—	—	—	—	3.0	0.03	—	—	3.03	1.0	—
8	1225	STD	—	—	—	—	—	74.6	0.05	—	—	74.65	20.0	—
9	1255	S	14.5	0.67	—	14.47	—	54.0	0.07	—	—	53.87	14.43	—
10	1255	40M	13.8	0.75	—	13.85	—	54.05	0.09	—	—	54.09	14.63	—
11	1106	S	11.5	0.83	—	11.63	—	11.80	0.10	—	—	11.80	12.91	—
12	1106	40M	11.5	0.92	—	11.72	—	11.89	0.12	—	—	11.89	13.11	—
13	1115	S	13.4	1.00	—	13.70	—	13.90	0.14	—	—	13.84	14.16	—
14	1120	S	16.5	1.08	—	16.88	—	17.13	0.16	—	—	17.06	15.69	—
15	1125	S	18.9	1.17	—	19.37	—	19.65	0.17	—	—	19.65	17.35	—
16	1130	S	19.1	1.25	—	19.65	—	19.94	0.19	—	—	19.94	17.14	—
17	1130	40M	19.0	1.33	—	19.63	—	19.92	0.21	—	—	19.92	17.28	—
18	1135	S	18.4	1.42	—	19.12	—	19.40	0.22	—	—	19.40	17.15	—
19	1140	S	19.0	1.50	—	19.80	—	20.09	0.24	—	—	20.09	17.29	—
20	1215	S	15.7	1.58	—	16.58	—	16.82	0.26	—	—	16.82	15.66	—
21	1220	S	15.0	1.67	—	15.97	—	16.20	0.28	—	—	16.20	15.13	—
22	1225	S	16.0	1.76	—	17.06	—	17.30	0.29	—	—	17.30	16.10	—
23	1230	S	16.0	1.83	—	17.13	—	17.38	0.31	—	—	17.38	15.94	—
24	1240	S	10.8	1.92	—	12.02	—	12.20	0.33	—	—	12.20	7.72	—
25	1245	S	5.4	2.00	—	6.70	—	6.80	0.34	—	—	6.80	7.67	—

APPENDIX B

NUTRIENT CONCENTRATION DATA

DATE	CRUISE	ONE	NUTRIENT	CONCENTRATION	DATA	19	APRIL	1972
TIME								
DEPTH								
DISTANCE								
SILICATE								
TOTAL								
NITRATE								
191149.	0.	0.87	22.09	16.94				
191151.	0.	1.09	21.99	17.66				
191153.	0.	1.31	22.12	17.89				
191155.	0.	1.53	22.14	18.08				
191159.	0.	1.97	22.25	18.17				
191201.	0.	2.19	22.27	18.36				
191203.	0.	2.40	22.29	18.47				
191205.	0.	2.52	22.42	18.53				
191207.	0.	2.76	22.43	18.65				
191209.	0.	3.00	22.45	18.66				
191211.	0.	3.24	22.45	18.77				
191213.	0.	3.48	22.45	18.82				
191215.	0.	3.60	22.45	18.82				
191217.	0.	3.60	22.45	18.82				
191219.	0.	3.60	22.45	18.82				
191304.	0.	4.20	22.45	18.82				
191306.	0.	4.40	22.45	18.82				
191308.	0.	4.60	22.45	18.82				
191310.	0.	4.80	22.45	18.82				
191312.	0.	4.83	22.45	18.82				
191314.	0.	4.88	22.45	18.82				
191316.	0.	4.88	22.45	18.82				
191318.	0.	4.90	22.45	18.82				
191330.	0.	5.00	22.45	18.82				
191342.	10.	5.10	22.45	18.82				
191404.	20.	5.30	22.45	18.82				
191416.	30.	5.40	22.45	18.82				
191428.	40.	5.70	22.45	18.82				
191438.	40.	5.70	22.45	18.82				
191448.	40.	5.95	22.45	18.82				
191448.	40.	6.20	22.45	18.82				

CRUISE TWO NUTRIENT CONCENTRATION DATA				28 APRIL 1972			
DATE	TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITRATE
2811055		0	0	16	1	14	0
2811106		0	1	15	1	12	0
2811115		0	2	19	1	13	0
2811120		0	2	20	1	15	0
2811125		0	3	22	1	16	0
2811130		0	3	22	1	16	0
2811135		0	3	22	1	16	0
2811140		0	3	22	1	16	0
2811145		0	3	22	1	16	0
2811215		0	7	19	1	15	0
2811220		0	8	17	1	14	0
2811225		0	8	19	1	15	0
2811230		0	10	13	1	15	0
2811240		0	11	7	1	17	0
2811245		0	11	7	1	17	0
2811300		0	11	7	1	17	0
2811305		0	11	7	1	17	0
2811310		0	11	7	1	17	0
2811315		0	11	7	1	17	0
2811320		0	11	7	1	17	0
2811325		0	11	7	1	17	0
2811330		0	11	7	1	17	0
2811335		0	11	7	1	17	0
2811340		0	11	7	1	17	0

CRUISE THREE			NUTRIENT CONCENTRATION DATA			5 MAY 1972	
DATE	TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITRITE
51	400.	0.	15.30	28.05	1.59	20.00	0.45
51	404.	0.	15.50	28.06	1.77	19.97	0.60
51	408.	50.	15.60	33.06	1.1.	24.70	0.0
51	412.	40.	15.70	33.09	1.86	25.57	0.0
51	416.	30.	15.90	31.87	1.1.	25.03	0.20
51	420.	20.	15.90	27.23	1.71	24.35	0.28
51	425.	10.	16.00	27.72	1.58	22.91	0.38
51	430.	0.	16.10	22.31	1.1.	19.55	0.40
51	435.	0.	16.60	16.94	1.82	19.55	0.40
51	440.	0.	17.60	27.01	1.73	22.68	0.45
51	445.	50.	18.20	19.01	1.1.	15.13	0.45
51	450.	0.	18.80	13.74	1.0.	12.87	0.45
51	455.	0.	19.00	13.53	1.0.	10.23	0.45
51	500.	0.	20.60	10.42	1.0.	17.35	0.40
51	505.	0.	20.60	10.71	0.0.	17.68	0.38
51	510.	0.	21.50	13.52	0.0.	19.75	0.55
51	515.	0.	21.50	13.56	1.1.	14.38	0.55
51	520.	0.	22.10	13.54	1.0.	13.39	0.45
51	525.	50.	22.10	13.94	1.0.	11.09	0.45
51	530.	0.	22.30	13.50	0.0.	11.09	0.58
51	535.	0.	23.30	13.42	1.0.	15.48	0.40
51	540.	0.	23.90	13.42	0.0.	10.84	0.40
51	545.	0.	24.50	13.28	0.0.	9.65	0.40
51	550.	0.	25.10	13.66	0.0.	9.65	0.35
51	555.	0.	25.50	13.91	1.0.	8.98	0.35
51	560.	50.	26.50	21.00	0.0.	19.30	0.30
51	565.	0.	26.70	20.00	0.0.	15.91	0.30
51	609.	50.	26.6.	15.06	1.1.	12.49	0.23

CRUISE FOUR NUTRIENT CONCENTRATION DATA 18-19 MAY 1972

[illegible]

CRUISE FOUR NUTRIENT CONCENTRATION DATA							18-19 MAY 1972	
DATE TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITRATE		
182340.	0.	15.58	19.64	1.13	19.60	0.25		
182350.	0.	15.91	19.30	1.14	19.87	0.25		
190000.	0.	15.25	19.98	1.11	19.76	0.31		
190010.	0.	16.66	20.99	1.12	19.87	0.31		
190020.	0.	17.97	20.98	1.15	19.57	0.25		
190030.	0.	17.48	20.09	1.11	19.53	0.25		
190040.	0.	17.83	20.09	1.18	19.57	0.25		
190050.	0.	18.15	20.29	1.12	19.63	0.23		
190100.	0.	18.99	17.61	1.10	18.28	0.25		
190110.	0.	19.26	17.19	1.06	18.09	0.25		
190120.	0.	20.00	7.19	0.86	18.09	0.45		
190830.	0.	0.00	7.08	0.86	10.09	0.45		
190840.	0.	0.00	7.43	0.89	10.50	0.44		
190850.	0.	0.00	7.17	0.92	12.07	0.43		
190910.	0.	0.00	7.31	0.91	10.87	0.40		
190920.	0.	0.00	7.43	0.88	10.74	0.42		
190930.	0.	0.00	8.09	0.85	10.29	0.42		
190940.	0.	0.00	8.43	0.77	10.87	0.42		
190950.	0.	0.00	8.75	0.78	10.23	0.40		
191000.	0.	0.00	8.88	0.78	10.35	0.40		
191010.	0.	0.00	8.65	0.88	10.52	0.42		
191020.	0.	0.00	8.55	0.88	10.53	0.42		
191030.	0.	0.00	8.08	0.86	10.87	0.41		
191040.	0.	0.00	9.43	0.80	10.53	0.41		
191050.	0.	0.00	9.83	0.90	10.85	0.38		
191100.	0.	0.00	9.58	1.04	10.53	0.38		
191110.	0.	0.00	9.32	1.09	10.20	0.36		
191120.	0.	0.00	9.58	1.09	11.11	0.36		
191130.	0.	0.00	9.66	1.00	11.11	0.36		
191140.	0.	0.00	9.22	1.09	11.11	0.38		
191150.	0.	0.00	9.74	1.05	11.11	0.37		
191200.	0.	0.00	10.72	1.05	11.11	0.37		
191210.	0.	0.00	10.61	1.00	12.21	0.33		
191220.	0.	0.00	10.99	1.08	12.63	0.33		
191230.	0.	0.40	10.61	1.04	12.88	0.33		
191240.	0.	1.00	10.57	1.10	12.31	0.33		
191245.	0.	1.30	10.57	1.10	13.19	0.33		
191255.	0.	2.52	19.14	1.10	14.80	0.33		
191300.	0.	0.00	1.14	1.10	14.80	0.33		

CRUISE FOUR NUTRIENT CONCENTRATION DATA				18-19 MAY 1972		
DATE/TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITRITE
191305.	0.	4.90	17.54	1.35	17.01	0.33
191310.	0.	5.70	17.99	1.35	17.21	0.33
191315.	0.	6.45	19.91	1.43	18.39	0.33
191320.	0.	7.20	19.01	1.38	17.87	0.33
191325.	0.	8.04	17.88	1.33	17.43	0.33
191330.	0.	8.98	18.33	1.22	17.32	0.31
1913340.	0.	10.56	15.62	1.20	16.83	0.29
1913350.	0.	12.24	15.28	1.15	15.32	0.23
191400.	0.	13.60	14.15	1.11	14.43	0.47
191410.	0.	15.20	13.47	1.12	14.01	0.47
191420.	0.	17.86	5.44	1.17	19.62	0.13
191430.	0.	19.67	0.0	1.43	4.42	0.11
191435.	0.	19.67	0.0	0.46	0.59	0.42
191440.	0.	20.49	0.0	0.22	2.87	0.33
191445.	0.	21.30	10.08	0.23	10.66	0.29
191450.	0.	23.15	1.71	0.87	13.18	0.37
191455.	0.	23.86	0.0	0.35	1.0	0.23
191500.	0.		0.0	0.35	0.0	0.44

CRUISE FOUR NUTRIENT CONCENTRATION DATA							19 - 21 MAY 1972
DATE TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITRATE	IE
191505	0	24.72	0.0	0.23	0.04	0.03	5
191510	0	25.43	0.0	0.15	0.16	0.31	3
191515	0	26.43	0.0	0.0	0.38	0.3	1
191520	0	27.28	0.0	0.27	0.69	0.4	7
191525	0	28.14	0.0	0.40	1.0	0.5	5
191530	0	29.00	0.4	0.51	2.4	0.5	2
191535	0	29.80	2.4	0.58	5.5	0.5	1
191540	0	31.70	7.2	0.66	8.8	0.5	5
191545	0	33.53	7.9	0.78	9.9	0.5	0
191550	0	35.37	8.0	0.80	9.4	0.5	0
191555	0	37.24	8.1	0.81	9.2	0.5	8
191600	0	39.17	8.5	0.84	9.9	0.5	7
191605	0	41.08	8.5	0.89	9.2	0.5	7
191610	0	43.01	8.5	0.88	9.5	0.4	9
191615	0	44.96	8.7	0.88	9.1	0.4	7
191620	0	46.88	8.7	0.88	8.8	0.4	8
191625	0	48.78	8.7	0.88	8.7	0.4	4
191630	0	50.65	8.7	0.88	8.6	0.4	4
191635	0	52.55	8.7	0.88	8.6	0.4	3
191640	0	54.45	8.7	0.88	8.6	0.4	7
191645	0	56.37	8.8	0.88	8.9	0.4	6
191650	0	58.28	8.8	0.88	9.2	0.4	0
191655	0	60.17	8.8	0.88	9.6	0.4	2
191700	0	62.05	8.9	0.88	12.7	0.4	3
191705	0	63.90	8.9	0.88	9.9	0.4	3
191710	0	65.75	10.2	0.88	10.9	0.4	3
191715	0	67.50	11.7	0.88	9.5	0.4	3
191720	0	69.35	13.7	0.88	11.7	0.4	3
191725	0	71.20	15.5	0.88	13.0	0.4	3
191730	0	73.05	17.5	0.88	15.5	0.4	3
191735	0	74.90	19.0	0.88	17.0	0.4	3
191740	0	76.75	20.0	0.88	18.8	0.4	3
191745	0	78.60	21.3	0.88	20.3	0.4	3
191750	0	80.45	22.5	0.88	22.0	0.4	3
191755	0	82.30	23.6	0.88	23.5	0.4	3
191800	0	84.15	25.0	0.88	25.9	0.4	3
191805	0	86.00	26.6	0.88	28.0	0.4	3
191810	0	87.85	28.3	0.88	30.4	0.4	0
191815	0	89.70	30.1	0.88	33.7	0.4	9
191820	0	91.55	32.0	0.88	37.2	0.4	3
191825	0	93.40	33.3	0.88	40.6	0.4	1
191830	0	95.25	35.1	0.88	43.6	0.4	7
191835	0	97.10	36.6	0.88	47.2	0.4	7
191840	0	98.95	38.1	0.88	50.6	0.4	7
191845	0	100.80	39.6	0.88	54.0	0.4	7
191850	0	102.65	41.1	0.88	57.4	0.4	7
191855	0	104.50	42.6	0.88	60.8	0.4	7
191900	0	106.35	44.1	0.88	64.2	0.4	7
191905	0	108.20	45.6	0.88	67.6	0.4	7
191910	0	110.05	47.1	0.88	71.0	0.4	7
191915	0	111.90	48.6	0.88	74.4	0.4	7
191920	0	113.75	50.1	0.88	77.8	0.4	7
191925	0	115.60	51.6	0.88	81.2	0.4	7
191930	0	117.45	53.1	0.88	84.6	0.4	7
191935	0	119.30	54.6	0.88	88.0	0.4	7
191940	0	121.15	56.1	0.88	91.4	0.4	7
191945	0	123.00	57.6	0.88	94.8	0.4	7
191950	0	124.85	59.1	0.88	98.2	0.4	7
191955	0	126.70	60.6	0.88	101.6	0.4	7
191960	0	128.55	62.1	0.88	105.0	0.4	7
191965	0	130.40	63.6	0.88	108.4	0.4	7
191970	0	132.25	65.1	0.88	111.8	0.4	7
191975	0	134.10	66.6	0.88	115.2	0.4	7
191980	0	135.95	68.1	0.88	118.6	0.4	7
191985	0	137.80	69.6	0.88	122.0	0.4	7
191990	0	139.65	71.1	0.88	125.4	0.4	7
191995	0	141.50	72.6	0.88	128.8	0.4	7
192000	0	143.35	74.1	0.88	132.2	0.4	7
192005	0	145.20	75.6	0.88	135.6	0.4	7
192010	0	147.05	77.1	0.88	139.0	0.4	7
192015	0	148.90	78.6	0.88	142.4	0.4	7
192020	0	150.75	80.1	0.88	145.8	0.4	7
192025	0	152.60	81.6	0.88	149.2	0.4	7
192030	0	154.45	83.1	0.88	152.6	0.4	7
192035	0	156.30	84.6	0.88	156.0	0.4	7
192040	0	158.15	86.1	0.88	159.4	0.4	7
192045	0	160.00	87.6	0.88	162.8	0.4	7
192050	0	161.85	89.1	0.88	166.2	0.4	7
192055	0	163.70	90.6	0.88	169.6	0.4	7
192060	0	165.55	92.1	0.88	173.0	0.4	7
192065	0	167.40	93.6	0.88	176.4	0.4	7
192070	0	169.25	95.1	0.88	179.8	0.4	7
192075	0	171.10	96.6	0.88	183.2	0.4	7
192080	0	172.95	98.1	0.88	186.6	0.4	7
192085	0	174.80	99.6	0.88	190.0	0.4	7
192090	0	176.65	101.1	0.88	193.4	0.4	7
192095	0	178.50	102.6	0.88	196.8	0.4	7
192100	0	180.35	104.1	0.88	200.2	0.4	7
192105	0	182.20	105.6	0.88	203.6	0.4	7
192110	0	184.05	107.1	0.88	207.0	0.4	7
192115	0	185.90	108.6	0.88	210.4	0.4	7
192120	0	187.75	110.1	0.88	213.8	0.4	7
192125	0	189.60	111.6	0.88	217.2	0.4	7
192130	0	191.45	113.1	0.88	220.6	0.4	7
192135	0	193.30	114.6	0.88	224.0	0.4	7
192140	0	195.15	116.1	0.88	227.4	0.4	7
192145	0	197.00	117.6	0.88	230.8	0.4	7
192150	0	198.85	119.1	0.88	234.2	0.4	7
192155	0	200.70	120.6	0.88	237.6	0.4	7
192160	0	202.55	122.1	0.88	241.0	0.4	7
192165	0	204.40	123.6	0.88	244.4	0.4	7
192170	0	206.25	125.1	0.88	247.8	0.4	7
192175	0	208.10	126.6	0.88	251.2	0.4	7
192180	0	210.00	128.1	0.88	254.6	0.4	7
192185	0	211.85	129.6	0.88	258.0	0.4	7
192190	0	213.70	131.1	0.88	261.4	0.4	7
192195	0	215.55	132.6	0.88	264.8	0.4	7
192200	0	217.40	134.1	0.88	268.2	0.4	7
192205	0	219.25	135.6	0.88	271.6	0.4	7
192210	0	221.10	137.1	0.88	275.0	0.4	7
192215	0	222.95	138.6	0.88	278.4	0.4	7
192220	0	224.80	140.1	0.88	281.8	0.4	7
192225	0	226.65	141.6	0.88	285.2	0.4	7
192230	0	228.50	143.1	0.88	288.6	0.4	7
192235	0	230.35	144.6	0.88	292.0	0.4	7
192240	0	232.20	146.1	0.88	295.4	0.4	7
192245	0	234.05	147.6	0.88	298.8	0.4	7
192250	0	235.90	149.1	0.88	302.2	0.4	7
192255	0	237.75	150.6	0.88	305.6	0.4	7
192260	0	239.60	152.1	0.88	309.0	0.4	7
192265	0	241.45	153.6	0.88	312.4	0.4	7
192270	0	243.30	155.1	0.88	315.8	0.4	7
192275	0	245.15	156.6	0.88	319.2	0.4	7
192280	0	247.00	158.1	0.88	322.6	0.4	7
192285	0	248.85	159.6	0.88	326.0	0.4	7
192290	0	250.70	161.1	0.88	329.4	0.4	7
192295	0	252.55	162.6	0.88	332.8	0.4	7
192300	0	254.40	164.1	0.88	336.2	0.4	7
192305	0	256.25	165.6	0.88	339.6	0.4	7
192310	0	258.10	167.1	0.88	343.0	0.4	7
192315	0	260.00	168.6	0.88	346.4	0.4	7
192320	0	261.85	170.1	0.88	349.8	0.4	7
192325	0	263.70	171.6	0.88	353.2	0.4	7
192330	0	265.55	173.1	0.88	356.6	0.4	7
192335	0	267.40	174.6	0.88	360.0	0.4	7
192340	0	269.25	176.1	0.88	363.4	0.4	7
192345	0	271.10	177.6	0.88	366.8	0.4	7
192350	0	272.95	179.1	0.88	370.2	0.4	7
192355	0	274.80	180.6	0.88	373.6	0.4	7
192360	0	276.65	182.1	0.88	377.0	0.4	7
192365	0	278.50	183.6	0.88	380.4	0.4	7
192370	0	280.35	185.1	0.88	383.8	0.4	7
192375	0	282.20	186.6	0.88	387.2	0.4	7
192380	0	284.05	188.1	0.88	390.6	0.4	7
192385	0	285.90	189.6	0.88	394.0	0.4	7
192390	0	287.75	191.1	0.88	397.4	0.4	7
192395	0	289.60	192.6	0.88	400.8	0.4	7
192400	0	291.45	194.1	0.88	404.2	0.4	7
192405	0	293.30	195.6	0.88	407.6	0.4	7
192410	0	295.15	197.1	0.88	411.0	0.4	7
192415	0	297.00	198.6	0.88	414.4	0.4	7
192420	0	298.85	200.1	0.88	417.8	0.4	7
192425	0	300.70	201.6	0.88	421.2	0.4	7
192430	0	302.55	203.1	0.88	424.6	0.4	7
192435	0	304.40	204.6	0.88	428.0	0.4	7
192440	0	306.25	206.1	0.88	431.4	0.4	7
192445	0	308.10	207.6	0.88	434.8	0.4	7
192450	0	310.00	209.1	0.88	438.2	0.4	7
192455	0	311.85	210.6	0.88	441.6	0.4	7
192460	0	313.70	212.1	0.88	445.0	0.4	7
192465	0	315.55	213.6	0.88	448.4	0.4	7
192470	0	317.40	215.1	0.88	451.8	0.4	7
192475	0	319.25	216.6	0.88	455.2	0.4	7
192480	0	321.10	218.1				

CRUISE FOUR NUTRIENT CONCENTRATION DATA							19 - 21 MAY 1972
DATE/TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITRATE	
200145.	10.	62.40	1.37	0.12	5.99	0.38	
200151.	20.	62.40	10.34	0.94	10.85	0.45	
200157.	30.	62.40	10.39	0.96	10.88	0.52	
200200.	40.	62.40	11.18	1.15	11.32	0.52	
200207.	50.	62.40	11.52	1.18	11.71	0.49	
200301.	60.	62.40	11.13	1.08	11.28	0.51	
200305.	7	62.40	13.94	1.64	22.80	0.34	
200335.	0.	62.65	3.64	0.72	6.49	0.34	
200340.	0.	62.85	4.64	0.73	7.41	0.36	
200345.	0.	63.10	6.90	0.78	8.61	0.36	
200350.	0.	63.30	8.90	0.87	9.55	0.43	
200355.	0.	63.60	10.00	0.87	10.55	0.36	
200400.	0.	63.85	10.28	0.87	10.63	0.38	
200405.	0.	64.10	10.28	0.87	10.63	0.38	
200410.	0.	64.35	10.28	0.87	10.63	0.38	
200415.	0.	64.60	10.28	0.87	10.63	0.38	
200420.	0.	64.85	10.28	0.87	10.63	0.38	
200425.	0.	65.10	10.28	0.87	10.63	0.38	
200430.	0.	65.35	10.28	0.87	10.63	0.38	
200435.	0.	65.60	10.28	0.87	10.63	0.38	
200440.	0.	65.85	10.28	0.87	10.63	0.38	
200445.	0.	66.10	10.28	0.87	10.63	0.38	
200450.	0.	66.35	10.28	0.87	10.63	0.38	
200455.	0.	66.60	10.28	0.87	10.63	0.38	
200500.	0.	66.85	10.28	0.87	10.63	0.38	
200505.	0.	67.10	10.28	0.87	10.63	0.38	
200510.	0.	67.35	10.28	0.87	10.63	0.38	
200515.	0.	67.60	10.28	0.87	10.63	0.38	
200520.	0.	67.85	10.28	0.87	10.63	0.38	
200525.	0.	68.10	10.28	0.87	10.63	0.38	
200530.	0.	68.35	10.28	0.87	10.63	0.38	
200535.	0.	68.60	10.28	0.87	10.63	0.38	
200540.	0.	68.85	10.28	0.87	10.63	0.38	
200545.	0.	69.10	10.28	0.87	10.63	0.38	
200550.	0.	69.35	10.28	0.87	10.63	0.38	
200555.	0.	69.60	10.28	0.87	10.63	0.38	
200557.	0.	69.85	10.28	0.87	10.63	0.38	
200600.	0.	70.10	10.28	0.87	10.63	0.38	
200603.	0.	70.35	10.28	0.87	10.63	0.38	
200606.	0.	70.60	10.28	0.87	10.63	0.38	
200607.	0.	70.85	10.28	0.87	10.63	0.38	
200610.	0.	71.10	10.28	0.87	10.63	0.38	
200615.	0.	71.35	10.28	0.87	10.63	0.38	
200620.	0.	71.60	10.28	0.87	10.63	0.38	
200625.	0.	71.85	10.28	0.87	10.63	0.38	
200630.	0.	72.10	10.28	0.87	10.63	0.38	
200635.	0.	72.35	10.28	0.87	10.63	0.38	
200640.	0.	72.60	10.28	0.87	10.63	0.38	
200645.	0.	72.85	10.28	0.87	10.63	0.38	
200650.	0.	73.10	10.28	0.87	10.63	0.38	
200655.	0.	73.35	10.28	0.87	10.63	0.38	
200657.	0.	73.60	10.28	0.87	10.63	0.38	
200700.	0.	73.85	10.28	0.87	10.63	0.38	
200705.	0.	74.10	10.28	0.87	10.63	0.38	
200710.	0.	74.35	10.28	0.87	10.63	0.38	
200715.	0.	74.60	10.28	0.87	10.63	0.38	
200720.	0.	74.85	10.28	0.87	10.63	0.38	
200725.	0.	75.10	10.28	0.87	10.63	0.38	
200730.	0.	75.35	10.28	0.87	10.63	0.38	
200735.	0.	75.60	10.28	0.87	10.63	0.38	
200740.	0.	75.85	10.28	0.87	10.63	0.38	
200745.	0.	76.10	10.28	0.87	10.63	0.38	
200750.	0.	76.35	10.28	0.87	10.63	0.38	
200755.	0.	76.60	10.28	0.87	10.63	0.38	
200760.	0.	76.85	10.28	0.87	10.63	0.38	
200765.	0.	77.10	10.28	0.87	10.63	0.38	
200770.	0.	77.35	10.28	0.87	10.63	0.38	
200775.	0.	77.60	10.28	0.87	10.63	0.38	
200780.	0.	77.85	10.28	0.87	10.63	0.38	
200785.	0.	78.10	10.28	0.87	10.63	0.38	
200790.	0.	78.35	10.28	0.87	10.63	0.38	
200795.	0.	78.60	10.28	0.87	10.63	0.38	
200800.	0.	78.85	10.28	0.87	10.63	0.38	
200805.	0.	79.10	10.28	0.87	10.63	0.38	
200810.	0.	79.35	10.28	0.87	10.63	0.38	
200815.	0.	79.60	10.28	0.87	10.63	0.38	
200820.	0.	79.85	10.28	0.87	10.63	0.38	
200825.	0.	80.10	10.28	0.87	10.63	0.38	
200830.	0.	80.35	10.28	0.87	10.63	0.38	
200835.	0.	80.60	10.28	0.87	10.63	0.38	
200840.	0.	80.85	10.28	0.87	10.63	0.38	
200845.	0.	81.10	10.28	0.87	10.63	0.38	
200850.	0.	81.35	10.28	0.87	10.63	0.38	
200855.	0.	81.60	10.28	0.87	10.63	0.38	
200860.	0.	81.85	10.28	0.87	10.63	0.38	
200865.	0.	82.10	10.28	0.87	10.63	0.38	
200870.	0.	82.35	10.28	0.87	10.63	0.38	
200875.	0.	82.60	10.28	0.87	10.63	0.38	
200880.	0.	82.85	10.28	0.87	10.63	0.38	
200885.	0.	83.10	10.28	0.87	10.63	0.38	
200890.	0.	83.35	10.28	0.87	10.63	0.38	
200895.	0.	83.60	10.28	0.87	10.63	0.38	
200900.	0.	83.85	10.28	0.87	10.63	0.38	
200905.	0.	84.10	10.28	0.87	10.63	0.38	
200910.	0.	84.35	10.28	0.87	10.63	0.38	
200915.	0.	84.60	10.28	0.87	10.63	0.38	
200920.	0.	84.85	10.28	0.87	10.63	0.38	
200925.	0.	85.10	10.28	0.87	10.63	0.38	
200930.	0.	85.35	10.28	0.87	10.63	0.38	
200935.	0.	85.60	10.28	0.87	10.63	0.38	
200940.	0.	85.85	10.28	0.87	10.63	0.38	
200945.	0.	86.10	10.28	0.87	10.63	0.38	
200950.	0.	86.35	10.28	0.87	10.63	0.38	
200955.	0.	86.60	10.28	0.87	10.63	0.38	
200960.	0.	86.85	10.28	0.87	10.63	0.38	
200965.	0.	87.10	10.28	0.87	10.63	0.38	
200970.	0.	87.35	10.28	0.87	10.63	0.38	
200975.	0.	87.60	10.28	0.87	10.63	0.38	
200980.	0.	87.85	10.28	0.87	10.63	0.38	
200985.	0.	88.10	10.28	0.87	10.63	0.38	
200990.	0.	88.35	10.28	0.87	10.63	0.38	
200995.	0.	88.60	10.28	0.87	10.63	0.38	
201000.	0.	88.85	10.28	0.87	10.63	0.38	
201005.	0.	89.10	10.28	0.87	10.63	0.38	
201010.	0.	89.35	10.28	0.87	10.63	0.38	
201015.	0.	89.60	10.28	0.87	10.63	0.38	
201020.	0.	89.85	10.28	0.87	10.63	0.38	
201025.	0.	90.10	10.28	0.87	10.63	0.38	
201030.	0.	90.35	10.28	0.87	10.63	0.38	
201035.	0.	90.60	10.28	0.87	10.63	0.38	
201040.	0.	90.85	10.28	0.87	10.63	0.38	
201045.	0.	91.10	10.28	0.87	10.63	0.38	
201050.	0.	91.35	10.28	0.87	10.63	0.38	
201055.	0.	91.60	10.28	0.87	10.63	0.38	
201060.	0.	91.85	10.28	0.87	10.63	0.38	
201065.	0.	92.10	10.28	0.87	10.63	0.38	
201070.	0.	92.35	10.28	0.87	10.63	0.38	
201075.	0.	92.60	10.28	0.87	10.63	0.38	
201080.	0.	92.85	10.28	0.87	10.63	0.38	
201085.	0.	93.10	10.28	0.87	10.63	0.38	
201090.	0.	93.35	10.28	0.87	10.63	0.38	
201095.	0.	93.60	10.28	0.87	10.63	0.38	
201100.	0.	93.85	10.28	0.87	10.63	0.38	
201105.	0.	94.10	10.28	0.87	10.63	0.38	
201110.	0.	94.35	10.28	0.87	10.63	0.38	
201115.	0.	94.60	10.28	0.87	10.63	0.38	
201120.	0.	94.85	10.28	0.87	10.63	0.38	
201125.	0.	95.10	10.28	0.87	10.63	0.38	
201130.	0.	95.35	10.28	0.87	10.63	0.38	
201135.	0.	95.60	10.28	0.87	10.63	0.38	
201140.	0.	95.85	10.28	0.87	10.63	0.38	
201145.	0.	96.10	10.28	0.87	10.63	0.38	
201150.	0.	96.35	10.28	0.87	10.63	0.38	
201155.	0.	96.60	10.28	0.87	10.63	0.38	
201160.	0.	96.85	10.28	0.87	10.63	0.38	
201165.	0.	97.10	10.28	0.87	10.63	0.38	
201170.	0.	97.35	10.28	0.87	10.63	0.38	
201175.	0.	97.60	10.28	0.87	10.63	0.38	
201180.	0.	97.85	10.28	0.87	10.63	0.38	
201185.	0.	98.10	10.28	0.87	10.63	0.38	
201190.	0.	98.35	10.28	0.87	10.63	0.38	
201195.	0.	98.60	10.28	0.87	10.63	0.38	
201200.	0.	98.85	10.28	0.87	10.63	0.38	
201205.	0.	99.10	10.28	0.87	10.63	0.38	
201210.	0.	99.35	10.28	0.87	10.63	0.38	
201215.	0.	99.60	10.28	0.87	10.63	0.38	
201220.	0.	99.85	10.28	0.87	10.63	0.38	
201225.	0.	100.10	10.28	0.87	10.63	0.38	
201230.	0.	100.35	10.28	0.87	10.63	0.38	
201235.	0.	100.60	10.28	0.87	10.63	0.38	
201240.	0.	100.85	10.28	0.87	10.63	0.38	
201245.	0.	101.10	10.28	0.87	10.63	0.38	
201250.	0.	101.35	10.28	0.87	10.63	0.38	
201255.	0.	101.60	10.28	0.87	10.63	0.38	
201260.	0.	101.85	10.28	0.87	10.63	0.38	
201265.	0.	102.10	10.28	0.87	10.63	0.38	
201270.	0.	102.35	10.28	0.87	10.63	0.38	
201275.	0.	102.60	10.28	0.87	10.63	0.38	
201280.	0.	102.85	10.28	0.87	10.63	0.38	
201285.	0.	103.10	10.28	0.87	10.63	0.38	
201290.	0.	103.35	10.28	0.87	10.63	0.38	
201295.	0.	103.60	10.28	0.87	10.63	0.38	
201300.	0.	103.85	10.28	0.87	10.63	0.38	
201305.	0.	104.10	10.28	0.87	10.63	0.38	
20							

CRUISE FOUR NUTRIENT CONCENTRATION DATA 19 - 21 MAY 1972

DATE/TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITR...
200810.	0.	73.40	0.0	0.24	1.16	0.19
200820.	0.	74.40	0.0	0.39	2.69	0.26
200830.	0.	75.40	0.0	0.46	3.74	0.29
200840.	0.	75.90	0.0	0.55	5.27	0.48
200848.	10.	76.00	0.0	0.54	5.18	0.41
200849.	20.	76.10	0.0	0.55	4.99	0.38
200851.	30.	76.20	0.0	0.55	5.74	0.38
200854.	40.	76.30	0.0	0.97	13.86	0.75
200856.	50.	76.40	0.0	1.21	18.77	0.70
200900.	60.	76.50	0.0	1.21	17.88	0.64
200904.	68.	76.60	0.0	1.56	15.88	0.34
200945.	0.	77.30	0.0	0.67	8.14	0.34
201000.	0.	77.90	0.0	0.69	8.56	0.34
201010.	0.	78.90	0.0	0.65	7.77	0.34
201020.	0.	81.00	0.0	0.60	7.77	0.34
201030.	0.	81.30	0.0	0.61	7.77	0.34
201040.	0.	81.45	0.0	0.61	7.77	0.34
201045.	0.	81.60	0.0	0.52	5.83	0.36
201050.	10.	81.75	0.0	0.60	5.03	0.36
201056.	20.	81.75	0.0	0.94	13.75	0.53
201100.	30.	81.90	0.0	1.01	13.75	0.53
201103.	40.	81.90	0.0	1.01	22.04	0.53
201107.	50.	82.10	0.0	1.01	22.04	0.53
201105.	60.	82.20	0.0	1.01	22.04	0.53
201116.	72.	82.30	0.0	1.01	22.04	0.53
201120.	0.	83.70	0.0	1.01	22.04	0.53
201200.	0.	83.70	0.0	1.01	22.04	0.53
201230.	0.	85.90	0.0	1.01	22.04	0.53
201240.	0.	86.90	0.0	1.01	22.04	0.53
201349.	5.	86.90	0.0	1.01	22.04	0.53
201356.	10.	86.90	0.0	1.01	22.04	0.53
201359.	20.	86.90	0.0	1.01	22.04	0.53
201403.	30.	86.90	0.0	1.01	22.04	0.53
201404.	35.	87.10	0.0	1.01	22.04	0.53
201416.	40.	87.10	0.0	1.01	22.04	0.53
201427.	50.	87.10	0.0	1.01	22.04	0.53
201430.	60.	87.10	0.0	1.01	22.04	0.53
201450.	72.	87.10	0.0	1.01	22.04	0.53
201500.	0.	87.10	0.0	1.01	22.04	0.53

CRUISE FOUR NUTRIENT CONCENTRATION DATA 19 - 21 MAY 1972

DATE/TIME	DEPTH	DISTANCE	SILICATE	PHOSPHATE	NITRATE	NITRITE
201510.	0.	88.68	0.0	0.22	0.07	0.07
201520.	0.	89.51	0.0	0.29	0.15	0.09
201530.	0.	90.35	0.85	0.56	1.82	0.17
201540.	0.	91.55	2.41	1.08	12.78	0.17
201557.	10.	91.55	3.27	0.64	12.20	0.17
201604.	20.	91.55	3.95	0.60	12.62	0.22
201607.	30.	91.55	4.54	1.21	12.81	0.22
201611.	40.	91.55	5.40	1.43	15.40	0.22
201615.	53.	91.55	6.53	1.41	14.88	0.23
201621.	60.	91.55	8.30	1.74	11.32	0.11
201715.	70.	92.40	10.29	1.83	14.34	0.11
201746.	0.	93.40	8.86	1.06	10.56	0.22
201800.	0.	94.20	8.70	1.08	9.51	0.22
201805.	0.	94.20	8.82	1.09	9.53	0.26
201809.	10.	94.20	8.47	1.03	9.08	0.23
201812.	20.	94.20	6.23	1.30	13.73	0.26
201815.	30.	94.20	5.25	1.67	13.83	0.34
201818.	40.	94.20	5.24	1.81	22.48	0.22
201824.	50.	95.50	5.44	1.65	6.67	0.26
201828.	60.	95.50	5.63	1.55	6.67	0.24
201845.	0.	96.10	6.43	0.93	6.05	0.24
201910.	0.	96.40	6.93	0.94	9.95	0.26
201920.	0.	96.50	7.17	0.95	9.95	0.29
201940.	0.	97.50	9.57	1.04	9.37	0.37
202026.	10.	97.50	6.62	1.03	15.80	0.55
202030.	20.	97.50	6.45	1.03	9.45	0.55
202049.	25.	97.50	6.43	1.03	9.45	0.55
202054.	30.	97.50	6.51	1.21	12.20	0.54
202100.	50.	97.50	8.51	1.68	18.45	0.61
202104.	60.	97.50	11.27	1.92	23.78	0.50
202108.	70.	97.50	16.69	2.80	34.48	0.44
202120.	0.	98.70	16.69	2.80	34.48	0.44
202130.	0.	98.70	16.69	2.80	34.48	0.44
202140.	0.	98.70	16.69	2.80	34.48	0.44
202150.	0.	98.70	16.69	2.80	34.48	0.44

CRUISE FOUR NUTRIENT CONCENTRATION DATA				19 - 21 MAY 1972		
DATE	TIME	DEPTH	SILICATE	PHOSPHATE	NITRATE	NITRITE
21	1129.	3.	18.10	1.29	13.76	0.31
21	1131.	10.	18.06	1.60	13.81	0.31
21	1133.	20.	17.97	1.50	13.79	0.31
21	1136.	30.	18.31	1.50	14.01	0.31
21	1139.	40.	20.44	1.64	15.55	0.31
21	1142.	50.	25.47	1.51	18.45	0.31
21	1145.	60.	26.50	1.80	17.69	0.31
21	1148.	77.	27.76	1.40	19.28	0.31
21	1200.	0.	17.35	1.37	13.00	0.00
21	1240.	0.	17.40	1.37	0.00	0.00
21	1245.	0.	17.51	1.36	0.00	0.00
21	1255.	0.	18.13	1.41	0.00	0.00
21	1300.	0.	18.09	1.40	0.00	0.00
21	1305.	0.	18.06	1.44	0.00	0.00
21	1310.	0.	19.35	1.47	0.00	0.00
21	1315.	0.	15.02	1.35	0.00	0.00
21	1325.	0.	15.57	1.25	0.00	0.00
21	1330.	0.	15.51	1.29	0.00	0.00
21	1336.	0.	16.81	1.64	0.00	0.00
21	1400.	10.	20.11	1.55	0.00	0.00
21	1406.	20.	21.19	1.56	0.00	0.00
21	1409.	30.	23.69	1.68	0.00	0.00
21	1411.	40.	29.88	1.88	0.00	0.00
21	1419.	50.	29.85	1.88	0.00	0.00
21	1422.	60.	16.37	1.29	0.00	0.00
21	1440.	70.	18.24	1.30	0.00	0.00
21	1445.	0.	18.89	1.11	0.00	0.00
21	1450.	0.	15.81	1.11	0.00	0.00
21	1455.	0.	15.91	1.11	0.00	0.00
21	1500.	0.	15.81	1.11	0.00	0.00

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ABSTRACT

Concentrations of silicate, phosphate, nitrate, and nitrite were determined in Monterey Bay, California. Data were collected aboard ship during four cruises in April and May 1972 using the Technicon[®] AutoAnalyzer[®] II System in dual channel operation. The sensitivity, reproducibility, and accuracy of this system were investigated and the results presented. Nutrient concentrations were presented as surface variations, depth variations, and vertical profiles. The large variability of nutrient concentrations in the ocean area studied was discussed. Upwelling areas were investigated for nutrient concentrations, circulation patterns, and variations in nutrient ratios. Planktonic bloom areas have been identified from the low nutrient levels, low nutrient ratio values, and high chlorophyll correlations. Results indicate that silicate was the limiting nutrient to biological activity in the waters studied. Assimilation ratios for biological activity were found to be 16.33 for NO₃:PO₄ and 21.14 for SiO₄:PO₄. Nutrient plateau regions were analysed and sources discussed. The major cause of nutrient concentration changes in the area (except plankton blooms) as determined from nutrient ratio studies was found to be circulation of the water masses.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
SEAWATER						
NUTRIENTS						
SILICATE						
PHOSPHATE						
NITRATE						
NITRITE						
ANALYSIS						
AUTOMATED						
CHEMICAL ANALYSIS						
AUTOANALYZER						
NUTRIENT RATIOS						
CENTRAL CALIFORNIA COAST						
NUTRIENT DISTRIBUTION						
CIRCULATION						
MONTEREY BAY, CALIFORNIA						
NUTRIENT TIME VARIATIONS						
NUTRIENT DEPTH VARIATIONS						
SEAWATER CHEMISTRY						
TECHNICON						
NUTRIENT VARIATIONS						
ORTHOPHOSPHATE						
INORGANIC NITRATES						
INORGANIC NITRITES						
REACTIVE SILICATES						
INORGANIC NITROGEN COMPOUNDS						
BIOLOGICAL POPULATION						
ASSIMILATION RATIOS						
BIOLOGICAL ASSIMILATION						
PLANKTON						
PLANKTON DISTRIBUTION						
PLANKTON BLOOMS						
CHLOROPHYLL DISTRIBUTION						



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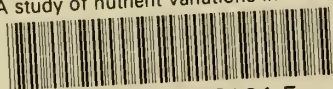
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